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Catalysis at Semiconductor Surfaces

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ABSTRACT

The final stages of the autoxidation of benzaldehyde at a germanium surface have been examined, to determine the composition of the final oxidation products. While the main product is benzoic acid, there is an appreciable amount of a stable peroxide, which appears to be dibenzoyl peroxide. Other possible products of the termination of the chain reaction, for example, benzil, were not detected.

The treatment of an etched germanium surface with an irradiated benzaldehyde film has been shown to produce a lower surface recombination rate. The photoelectromagnetic method was used for these measurements, and the simplified procedure followed was sufficient for comparative purposes, although not rigorous enough for the accurate measurement of absolute values. It was deduced that the reduction in the surface recombination velocity resulted from an increase in the surface barrier height, brought about by the oxidising action of the benzaldehyde. This conclusion was supported by the findings of the 1962 program, in which improvements in the rectification characteristics of surface-barrier diodes were also attributed to an increase in the surface barrier, following the same treatment. It was concluded that the irradiated benzaldehyde treatment would be valuable for the final processing of the surfaces of semiconductor devices, particularly as it would also tend to clean the surface of metallic contamination.

An enhanced photoelectric effect has been observed after applying a benzaldehyde film to a surface-barrier diode on n-type germanium. Using the theory of charge transfer catalysis, it has been found possible to correlate the quantum yield of the reaction with the increase in efficiency of the photoelectric effect. The quantum yield in the photooxidation of a thin film of benzaldehyde is between 7 and 9, and the maximum corrected increase in efficiency from the photo-electric effect is about 6 times, which shows reasonable agreement with the theory.

(ii)

It has not been possible to confirm the high surface potentials for germanium in wet oxygen, recorded in the 1962 program, and it is probable that errors resulted from the indirect null-method of measuring the potentials. It is still possible to measure potentials of the order of 10 volts at infrequent intervals, but the method of generation of such potentials is not known. Reliable and consistent measurements of the normal surface potentials, between 500 and 700 mV in wet oxygen, have been made using a new technique with a glass fibre probe, in conjunction with an electrometer voltmeter having an input resistance of 10^{16} ohms. The glass fibre system is able to probe the surface layer of the germanium without producing any mechanical or electrical disturbance of the surface. Interesting effects have been observed by varying the ambient and introducing a short circuit or an applied potential across the electrode system. The decay curve of the potential on removal of the water vapour is interpreted as a measure of the time of relaxation of slow surface states in the oxide layer, of between 300 and 500 seconds, and a step-like structure, sometimes observed, may be related to irregularities in the oxide structure or to a spectrum of energy levels. An oscillatory behaviour of the potential, following a short circuit, has been explained in terms of a non-equilibrium distribution of water molecules at the surface, in conjunction with the diffusion time of holes in the oxide layer, and adjustments of the space-charge potential. The concentration of slow states at a germanium surface calculated from the observed potentials, is between 3 and 4×10^{13} per cm^2 .

There are indications that the probe technique developed may also be useful in studying the properties of oxide films on metals.

CONTENTS

	<u>Page</u>
1.0 <u>Introduction</u>	1
2.0 <u>Outline of the Experiments</u>	2
3.0 <u>Experimental Details - Chemical</u>	7
3.1 Apparatus	7
3.2 Materials	8
3.3 Procedure	9
3.4 Detection of benzoic acid on the gas chromatograph	10
3.5 Detection of perbenzoic acid on the gas chromatograph	11
3.6 Detection of final oxidation products on the gas chromatograph	11
3.7 Detection of final oxidation products by chemical methods	12
3.8 Determination of perbenzoic acid	13
4.0 <u>Experimental Details - Physical</u>	14
4.1 Contact potential tests	14
4.1.1 Apparatus	14
4.1.2 Procedure	14
4.2 Confirmatory experiments on earlier potential measurements	15
4.3 Potential measurements with the E.I.L. Model 33C	21
4.4 Potential measurements with the Wayne-Kerr M.141	23
4.5 Potential readings with continuous recording from the Wayne-Kerr M.141 and using a glass fibre probe	29
4.6 Measurement of surface recombination rate by the Photoelectromagnetic effect	31
4.6.1 Apparatus	31
4.6.2 Procedure	31
4.6.3 Principles of the method	31
4.6.4 Measurements of the photoelectromagnetic effect and the influence of benzaldehyde treatment	35
4.7 Measurement of the effect of benzaldehyde on photoelectric current output from surface barrier diodes	38

	<u>Page</u>
4.7.1 Apparatus	38
4.7.2 Procedure	39
5.0 <u>Discussion of Chemical Results</u>	45
5.1 Evidence for a number of reaction products of the benzaldehyde oxidation	45
5.2 Interpretation of results obtained	48
5.2.1 Detection of benzoic acid and perbenzoic acid on the gas chromatograph	48
5.2.2 Variation in concentration of perbenzoic acid	48
5.2.3 Detection of other oxidation products	48
6.0 <u>Discussion of Physical Results</u>	49
6.2 Surface recombination rate	49
6.3 Photoelectric effects	52
6.4 Surface potential measurements	59
6.4.1 Appraisal of the experiments reported in 1962	59
6.4.2 Evaluation of the accuracy of voltage measurements by the null method	61
6.4.6 Potential and band structure relationships	63
6.4.8 Discussion of experimental results	70
7.0 <u>Conclusions</u>	75
8.0 <u>References</u>	78

1.0. INTRODUCTION.

1.1. The present account is a continuation of the work reported in the Final Technical Report 1962, under Contract No. DA - 91 - 591 - EUC - 1698.

1.2. It was well known that benzaldehyde produced peroxides in an autoxidation process when exposed to light in the presence of oxygen, (1, 2, 3, 4) and the active oxidizing agent had been used for the preparation of acetyl benzoyl peroxide by mixing benzaldehyde with acetic anhydride before irradiation (5, 6.).

1.3. In the Final Report, 1962, the chemical and physical changes taking place at a germanium crystal surface, in the presence of a film of benzaldehyde and ultraviolet irradiation, were examined. The chemical reactions were studied, to determine whether the semiconductor surface had any catalytic action, either positive or negative, and whether this action was influenced by dislocation concentration or an excess of donor or acceptor centres in the bulk of the crystal. The electrical measurements were designed to measure any physical changes in the surface layer of the semiconductor after photochemical treatment, and observations of rectification efficiency at surface barrier contacts and of surface charge were made.

1.4. It was concluded that the benzaldehyde was oxidized to benzoic acid with a quantum yield of about 7 in 366 mμ radiation, and that the oxidation was a 1st order reaction after the first few minutes. No significant difference in reaction rate was found between the surfaces of n-type germanium, p-type germanium or glass, suggesting that the germanium was showing no specific catalytic activity. The reaction rate was similar for both ground and etched surfaces, indicating that dislocation density did not influence the reaction. All surfaces behaved as negative catalysts, by removing the chain-carrying radicals produced in the irradiation.

1.5. The electrical measurements showed that the treatment of n-type germanium surfaces with an irradiated film of benzaldehyde improved the reverse impedance of surface-barrier rectifying contacts. The effect was apparently produced by free radicals or peroxides, which, it was suggested, created a permanent increase in the number of surface states, or a modification of the structure or thickness of the surface oxide layer.

1.6. Large electrostatic charges were observed at the surfaces of n-type germanium in an atmosphere of wet oxygen or argon. During measurements of contact potential, voltages of up to 100

were observed in some cases. The formation of the potential was assisted by pre-treatment of the surface with an irradiated film of benzaldehyde. High potentials were more difficult to obtain on p-type germanium or p-type silicon. The magnitude of the potential was difficult to explain, but appeared to be derived from positive charges at the oxide-gas interface, induced by the adsorption of water molecules. Charge accumulation was not found to be responsible.

1.7. The affinity of the germanium surface for electron-donor molecules, of water, for example, and the failure to produce specific catalytic effects in the oxidation of benzaldehyde, demonstrated that the surface was predominantly an electron-accepting catalyst. This condition is the result of the high concentration of slow acceptor states at the oxide-gas interface, which controls the catalytic behaviour.

1.8. Some brief observations were made of the high photo-currents produced at a point contact rectifier in the presence of benzaldehyde and stabilizing agents and it appeared that complex chemical and physical processes might be involved.

1.9. In the continuation of the work, it was decided that it would be helpful to confirm, if possible, the formation of perbenzoic acid during the irradiation of the benzaldehyde film and also identify the other products of reaction; the final amount of benzoic acid produced was about 20% less than the theoretical value, based on the decomposition of the benzaldehyde. The physical measurements required a more critical examination, and more accurate measurements of the high potentials previously recorded at the semiconductor surfaces in wet oxygen. It was decided to compare the effect of benzaldehyde in activating the germanium surface for rectifying contacts with its effect on surface recombination rate, using the photomagneto electric effect. It appeared likely that the new program of measurements might provide further useful information on slow surface states at the oxide-gas interface, and give a better evaluation of the applicability of the benzaldehyde treatment to semiconductor devices. More detailed measurements of the photoelectric effect in the presence of benzaldehyde were required, which might show correlations with the chemical and physical data already obtained.

2.0. OUTLINE OF THE EXPERIMENTS.

2.1. Chemical work.

2.1.1. Following similar procedures to the earlier work, single crystal samples were used in all the experiments and reactions were carried out on prepared (1.1.1.) surfaces in an oxygen atmosphere. The area of crystal surface available for

reaction varied between 1 cm^2 and 3 cm^2 , depending on the sample used. Both germanium and silicon crystal samples were available for testing.

2.1.2. The main objectives of the work were to confirm the variation in the concentration of perbenzoic acid during the oxidation of benzaldehyde and to identify, if possible, the other final reaction products, apart from benzoic acid.

2.1.3. The Final Report 1962 has described the estimation of the total acid formed (computed as benzoic acid) by a titration method. The reaction products were washed from the surface of the germanium with acetone, and after admixture with water were titrated electrometrically with sodium hydroxide solution. Full details are given in Sect. 3.3.7. and Sect. 3.5 of that report. Typical titration curves, illustrated in Fig. 22 of the same report, revealed the presence of two acidic components in the product, as shown by a double inflection in the curve. The double inflection was most pronounced when titrating the products of the first few minutes of irradiation and had completely disappeared after 50 minutes of irradiation. Comparison with a blank curve and a curve for pure benzoic acid, suggested that the acid formed in the intermediate stages of the reaction was a stronger acid, with an end point at a lower potential than benzoic acid. It was concluded that the compound was probably perbenzoic acid, as this was known to be the first stable product of irradiation.

2.1.4. It was decided to attempt to confirm the presence of the two separate acids by an independent method, and to observe their variation in concentration as the reaction proceeded. The only alternative method of carrying out this estimation which was available (in view of the very small quantities involved) was the gas chromatograph. However, as detailed in Sect. 2.1.3. of Final Report 1962, we had experienced difficulties in estimating benzoic acid in our apparatus, and had concluded that high temperatures above 220°C . were necessary to obtain elution of the acid in a reasonable time. Oxidation of benzaldehyde and decomposition of perbenzoic acid would both be rapid at the high temperature, and it appeared unlikely that meaningful figures would be easy to obtain. It was clear that further investigation and development of the method for benzoic acid on the gas chromatograph was essential before any further progress could be made. In these investigations, the use of shorter columns and different stationary phases were investigated, and it was found that temperatures of 220°C . or higher were not in fact necessary.

2.1.5. In Sect. 5.2.11 of Final Report 1962, it was shown that in the oxidation of benzaldehyde at an irradiated germanium surface, the final amount of benzoic acid produced was 23.5% less than the theoretical value, based on the amount of benzaldehyde consumed. It was considered that benzoin, dibenzoyl peroxide and benzil were other possible products of the reaction. All these compounds have high boiling points and it was necessary to operate the gas chromatography column above 200°C. to provide a chance of eluting them within a reasonable time. The column used for these experiments was shortened from 240 cm. to 60 cm., which, together with a higher gas flow rate and the use of silicone high vacuum grease as the stationary phase, greatly decreased the retention time for compounds of low volatility.

2.1.6. For the detection of perbenzoic acid, benzoin, dibenzoyl peroxide and benzil, the irradiated material was washed from the crystal surface with small quantities of chloroform, not exceeding a total of 5 ml. The solution volume was standardized at 5 ml. in each experiment, as this was about the minimum quantity which would ensure a complete washing of the sample. Even so, the sample concentration was rather small considering that only 1 microlitre of solution could be injected into the gas chromatograph; this increased the difficulty of detecting minor constituents of the sample.

2.1.7. Other confirmatory chemical reactions were available to support the gas chromatography work. For example, the liberation of iodine from acid potassium iodide solution would show the presence of peroxides, i.e., perbenzoic acid early in the irradiation period, or benzoyl peroxide in the final oxidation products. Benzoin could be detected by the sensitive fluorescent reactions with boron or silicon solutions. (7, 8, 9, 10.).

2.1.8. The ultra-violet radiation, in the range 365-366 mμ was provided by a Hanovia 250 watt mercury lamp, fitted with a double black glass filter. For the absolute measurement of radiation intensity a chemical actinometer was used, utilizing the isomerisation of *o*-nitrosobenzoic acid, which has a quantum yield of 0.5. This measurement is fully described in Sect. 3.3.8, Final Report 1962. For routine purposes, radiation intensity was usually measured with a photocell and microammeter.

2.1.9. All chemical measurements were carried on the etched surface of one sample of n-type germanium crystal, as previous work had revealed that the doping of the crystal or the dislocation density had no significant effect on the progress of the chemical reaction.

2.2. Physical Measurements.

2.2.1. A more detailed examination of the formation of the high potentials, previously recorded during contact potential measurements, was one of the main objectives of the physical studies. It was also decided that it would be valuable to measure the effect of benzaldehyde treatment on the surface recombination rate at an etched surface; such data would be complementary to the results of rectification measurements, previously reported, and would provide additional evidence for evaluating the benzaldehyde process for the final surface treatment of semiconductor devices. Further experiments were required on the generation of photoelectric voltages at rectifying point contacts in the presence of benzaldehyde: it was considered that a theory which would explain the effects produced might also be helpful in verifying the chemical observations.

2.2.2. Because of the unusually high values recorded in the contact potential experiments, some doubts were felt about the method of generation of these potentials and their interpretation. It was regarded as essential to make further careful tests of the existing measuring equipment and to take steps to obtain more accurate apparatus, on which direct readings of the polarity and magnitude of the voltages could be taken.

2.2.3. The original contact potential apparatus used a fixed platinum reference electrode, very closely spaced from the surface being measured. The potential picked up by the electrode was fed into a vibrating capacitor, to convert it to an a.c. voltage, following the technique of Palevsky et al. (11), and the voltage was amplified and displayed on an oscilloscope. This method of measurement was not direct reading, nor was there any direct indication of the polarity of the voltage; both amplitude and polarity had to be determined by using a backing-off voltage from a potentiometer network. The response time of the input circuit, including the backing-off network, was slow, making it difficult to follow a rapidly changing voltage.

2.2.4. A series of repeat experiments was first carried out on the original contact potential apparatus, following the same technique described in Sect. 4.9, Final Report 1962. Germanium surfaces were prepared by etching in sodium perborate solution or CPI etch. (CPI etch is prepared from 30 ml. conc. HF, 50 ml. conc. HNO_3 , 30 ml. glacial acetic acid and 0.07 g. I_2). The surfaces were exposed to the well known dry oxygen-wet oxygen cycle, originated by Brattain and Bardeen (12, 13) and potential changes were recorded; the effect of treating the surface with an irradiated benzaldehyde film was also studied.

As the results obtained were less promising than those obtained in the first series of experiments, further work was continued using commercial equipment, the E.I.L. Vibron Electrometer Model 33C (manufactured by Electronic Instruments Ltd., Richmond, Surrey, England).

2.2.5. A new electrode assembly was used in conjunction with the E.I.L. electrometer. This instrument was still not ideal for this investigation, as it had a maximum reading of only one volt, and therefore a backing-off circuit was still required: while the high input impedance was useful, it produced a very slow response to changes in the backing-off potential. A further series of experiments was carried out with the E.I.L. Model 33C to investigate methods of generating high potentials at the electrodes, and the effect of foreign particles in the electrode gap (e.g. fibres and water droplets). Readings on the E.I.L. instrument were also compared directly with those obtained on the original measuring equipment.

2.2.6. At the time the E.I.L. instrument was being used there was no equipment on the market for the direct measurement of D.C. potentials up to 100 volts with an input resistance of 10^{13} to 10^{16} ohms. One of the objectives of the new work was to couple a direct-reading instrument to a recorder and obtain more accurate records of the rise and decay of the potentials as damp oxygen was introduced. Suitable equipment was under development by both E.I.L. and Wayne-Kerr Ltd., (New Malden, Surrey, England) and steps were taken to obtain the Wayne-Kerr Precision Electrometer M 141 as early as possible. Unfortunately, due to production difficulties, this instrument was not available until the last few weeks of the contract, although it was possible to carry out a number of useful measurements, including the rate of generation and decay of the surface potentials.

2.2.7. To provide further information on the effect of benzaldehyde on surface properties, surface recombination rate measurements were carried out using the photoelectromagnetic effect (14)(15). Thin samples of germanium were provided with two ohmic contacts on one face and the sample, with connecting leads, was mounted in a block of "Araldite", leaving the plain face exposed. The exposed face was then ground and chemically polished and the sample was mounted between the poles of a permanent magnet. Illumination of the sample by a projector lamp and measurement of the open-circuit voltage enabled an estimate of the surface recombination rate to be made. Further measurements on the crystal surfaces after treatment with an irradiated benzaldehyde film enabled the possible effect of the treatment on semiconductor devices to be evaluated.

2.2.8. It was hoped that a further study of the photoelectric phenomena, observed at a point contact in the presence of benzaldehyde, might provide additional information on the chemical reactions which were being studied. Further measurements were carried out on the magnitude and duration of the photoelectric currents obtained in the presence of benzaldehyde and with the addition of various stabilizing compounds. The theoretical explanation of the results obtained was correlated with the information given by the chemical, contact potential, rectification and surface recombination measurements.

3.0 EXPERIMENTAL DETAILS - CHEMICAL

3.1. Apparatus

3.1.1. The apparatus used for the irradiation of samples was essentially the same as previously described in Final Report 1962, and is illustrated in Fig. 1. It consisted of a polythene container with a "Perspex" cover (transparent to 366 mμ radiation) and supported the prepared crystal sample in a glass funnel, in a horizontal position. At the end of the reaction, a plug was removed from the lid of the vessel and the film of benzaldehyde was washed from the crystal surface with solvent, using a glass syringe. The washings were collected under the reaction vessel in a standard flask. Oxygen was supplied through the lid and escaped via the funnel tubulation.

3.1.2. A 250 watt Hanovia mercury lamp was placed vertically above the reaction vessel, so that the distance between the quartz burner and the sample surface was 30 cm. in each experiment. A double black glass filter was fitted to the lamp shield and transmitted radiation almost exclusively in the 365-366 mμ region. The lamp was run for about 15 minutes before the start of each experiment, so that stable operating conditions were attained, and forced air cooling was used to avoid any erratic behaviour of the mercury arc due to overheating. Comparative readings of the lamp output were made before each experiment with a photoelectric illumination meter, G.E.C. type M.903, which uses a selenium photocell. These readings could be referred to absolute measurements, determined by a chemical actinometer, using the isomerisation reaction of o-nitrobenzaldehyde to o-nitrosobenzoic acid. The absolute measurements are described in detail in Final Report 1962, Sect. 3.3.8. and Sect. 3.6.

3.1.3. The gas chromatographic equipment was the same as employed for the previous work, and consisted of a 240 cm. column, 4 to 5 mm. internal diameter, packed with 60-80 mesh celite, impregnated with the stationary phase.

The stationary phase was varied to suit the temperature and the separation required. For all temperatures up to about 200°C, 15% Apiezon M grease was a good general-purpose material on 60-80 mesh celite: for temperatures above 200°C, and if a smaller retention time was required, 15% silicone high-vacuum grease was found to be useful. The column length could be reduced to 180 cm., 120 cm. or 60 cm., as required, to decrease the retention time for compounds with low volatilities. The temperature of the column was controlled by a vapour jacket using a liquid of suitable boiling point. Samples of liquid, up to 1 μ l in volume were injected at the start of the column through a serum cap of silicone rubber and into a flash heater, operating at about 180°C. The carrier gas was argon and the detector was a standard argon ionization (Loveloek) pattern, operating at 1500 v. and feeding an amplifier and pen recorder.

3.2. Materials

3.2.1. In most of the experiments, benzaldehyde, Analar grade, as manufactured by British Drug Houses was used. The earlier work on the rate of formation of benzoic acid, as reported in Sect. 3.3, Final Report 1962, had called for some purification of the benzaldehyde, to eliminate possible traces of stabilizers. The benzaldehyde had been redistilled in a stream of deoxygenated hydrogen and stored in a tightly stoppered brown glass bottle, in the dark, before being used. It had been found, however, that under the conditions of our experiments, the purification had no significant influence on the reaction kinetics: this was undoubtedly due to the predominant influence of the surface as a recombination region for the free radicals formed during irradiation. For the study of the composition of the final reaction products, it was not, therefore, considered necessary to make any further purification.

3.2.2. All experiments were carried out on a prepared (1.1.1.) plane of an n-type germanium crystal sample, resistivity 2.5 ohm-cm., antimony doped. The area of the crystal surface was approximately 4 cm². After cutting, the surface was first ground with 250 mesh carborundum, then 600 mesh carborundum. A clean etched surface was obtained by placing the sample in a mixture of 20 ml. water and 5 g. sodium perborate and heating to about 80°C for 5 minutes. This procedure provided an uncontaminated surface by etching away a thin layer of material without excessive polishing action or formation of a thick oxide film.

3.2.3. Previous work had shown that the course of the reaction was not influenced by the conductivity type of the germanium or the surface preparation, so no variations in the test sample were made in the present work.

3.3. Procedure

3.3.1. The crystal surface was prepared as described in Sect. 3.2.2. and the sample placed in position in the reaction vessel. The transparent lid was fitted and the oxygen flow started at a rate of about 500 ml./min. The U.V. lamp was switched on for 15 minutes, to reach a stable operating temperature, and the radiation was measured.

3.3.2. The benzaldehyde sample was then added to the surface from a micro-pipette, by removing the plug in the lid. A sample volume of 0.05 ml. was correct for providing a thin film over the whole surface of the sample, whose area was 4 cm².

3.3.3. At the end of the irradiation time, the lamp was switched off and the organic material was rapidly washed from the crystal surface with four 1 ml. portions of chloroform from a glass syringe, the washings being collected in a 5 ml. calibrated flask below the funnel. The present work was concerned with identifying perbenzoic acid and looking for other final oxidation products, such as benzoin, benzil or benzoyl peroxide, and it was not considered to be desirable to make any addition of hydroquinone to the sample. This compound had been added when estimations of benzaldehyde and benzoic acid were being made, to suppress any further oxidation of the benzaldehyde after the experiment: it was considered that in the present work it might give rise to undesirable side reactions. The volume of sample was made up to 5 ml. with chloroform in each case.

3.3.4. A 1 µl. sample was taken by a Hamilton microsyringe from each solution and injected into the gas chromatograph. A sample of 1 µl. is normally regarded as large by gas chromatographic standards and most organic compounds will give a very high output at the detector for this concentration: larger samples tend to overload the conventional analytical column and produce a broadening of the peaks and poor peak separations. However, in the present estimations, the samples were considerably diluted in preparation. No more than 0.05 ml. of benzaldehyde could be used to provide the thin film on the area of crystal surface available, and no less than 3 or 4 ml. of solvent could be employed for washing purposes, to ensure the removal of all the sample. The low concentration of the sample and the known low sensitivity of the detector to certain organic species (e.g. benzoic acid) added to the difficulties of detecting the compounds we were seeking.

3.4. Detection of benzoic acid on the gas chromatograph.

3.4.1. It was clear, from our previous difficulties in detecting benzoic acid in the irradiated samples on the gas chromatograph, that some development of the technique was needed before we could proceed to look for other compounds. As described in Final Report 1962, Sect. 2.1.3, it appeared that a high column temperature of about 220°C . was required to elute benzoic acid within a reasonable time, at the argon flow of 28 ml./min. then being used. Under these conditions, a small peak with a retention of time of about 50 minutes had been attributed to benzoic acid. The height of the peak was very small, partly due to the spreading of the zone by diffusion during the long retention on the column, and the identification was very inconclusive. At the high temperature there was little separation of the chloroform, benzaldehyde, or the marker compound, *o*-dichlorobenzene, and these all appeared close to the start of the chromatogram.

3.4.2. More experiments were carried out on the standard 240 cm. column, packed with 60 · 80 mesh celite/15% Apiezon M as stationary phase and at a temperature of 212°C . Samples of a saturated methanol solution of benzoic acid were added; apart from the large solvent peak at the beginning, no significant peaks which might be attributed to the acid were found after 60 minutes elution, using a gas flow of 28 ml./min.

3.4.3. The column temperature was then reduced to 110°C . (using toluene for the vapour jacket), in case we had underestimated the volatility of benzoic acid at this temperature; (the boiling point is 249°C .). Immediately, more promising results were obtained and well-defined peaks were observed. The elution time for benzoic acid at this temperature was only slightly longer than that of the standard substance *o*-dichlorobenzene, which is clear from a comparison of the chromatogram in Fig. 2 with that in Fig. 3, which is for a benzaldehyde estimation on the same time scale.

3.4.4. However, Fig. 3 and similar chromatograms for samples with long irradiation periods, showed no indication of benzoic acid peaks at the appropriate place, even when the maximum sensitivity of the apparatus was employed. At maximum sensitivity some base line irregularities were always present, and, therefore, small peaks would not easily be detected. It was concluded that while benzoic acid was eluted in a normal manner at a column temperature of 110°C ., the sensitivity of the detector was very low for this compound, making detection very difficult in the small samples used for our experiments. In contrast, the sensitivity for benzaldehyde is very good and the reason for the very large

sensitivity difference for a very small change in structure is not clear.

3.5. Detection of perbenzoic acid on the gas chromatograph

It was likely that perbenzoic acid might have a volatility similar to or higher than that of benzoic acid, (its melting point is 43°C) and so the same operating conditions at 110°C were used for the gas chromatography column. Apart from the possible low sensitivity, other difficulties were expected because of the instability and reactivity of the compound at 110°C : a lower temperature was not desirable, as this would increase the retention time, during which reaction with the column packing could take place.

3.5.2. A number of samples were prepared by irradiating benzaldehyde for short periods on the crystal surface. Irradiation times of 2 to 5 minutes were in the region where the concentration of the per-acid appeared to reach a maximum. No peaks which could be attributed to perbenzoic acid or benzoic acid could be found. It was shown that these samples contained an oxidising agent, probably the per-acid, by mixing with an acetone-water mixture containing a little acidified potassium iodide and starch solutions: the liberation of iodine by the oxidising agent was indicated by the blue colour produced.

3.6. Detection of final oxidation products on the gas chromatograph

3.6.1. Published information suggested that in addition to benzoic acid, benzil and dibenzoyl peroxide were possible final products of the oxidation of benzaldehyde, and there was also some probability of benzoin being formed.

3.6.2. Of these compounds, benzil boils at 348°C , benzoin at 344°C and dibenzoyl peroxide decomposes on melting at 105°C . A short, high temperature column was required for this work, and it was therefore shortened to 60 cm. The column was packed with 15% silicone high vacuum grease on 60-80 mesh celite as the stationary phase, and the temperature raised to 213°C (ethyl benzoate as the boiling liquid). The short column enabled a higher flow rate of the carrier gas of 40 ml/min. to be used, without any large pressure differential across the column.

3.6.3. Evidently dibenzoyl peroxide would decompose on injection into the column, but could be identified by emerging as benzoic anhydride, boiling point 360°C . Samples which had been irradiated for about 60 minutes to give an almost complete reaction were injected into the column, in benzene solution. In none of the experiments were any peaks attributable to compounds of high boiling point discovered. Each chromatogram ran for a period of about 2 hours. It was considered to be unlikely that all the compounds being sought would have very low detection efficiencies in the manner of benzoic acid, and the most likely reason for the failure was the low volatility at 213°C .

3.6.4. The upper limit of operation of the existing chromatograph was about 250°C . for various reasons connected with the vapour jacket design, and it appeared that a temperature of about 300°C . might be needed. An attempt was made to reduce retention time at 213°C . by using a glass bead column, consisting of 0.177 mm. (A.S.T.M. Grade 80) beads coated with 0.06% by weight of Apiezon M grease. Glass bead columns have been recommended for giving shorter retention times and sharper peaks, without loss of resolution (16, 17, 18). However, we experienced difficulty with blockages in these columns, except at extremely small concentrations of stationary phase, and the columns appeared to be overloaded by 1 μl samples.

3.7. Detection of final oxidation products by chemical methods.

3.7.1. The gas chromatographic approach having proved unsatisfactory, chemical methods of detection were used. An oxidising agent was shown to be present in the solid product of 120 minutes irradiation of benzaldehyde, by a red coloration in the ferrus thiocyanate test. Perbenzoic acid had disappeared after this period of irradiation, and the reaction was most likely to have been produced by dibenzoyl peroxide. A solution of the final product in acetone, when added to an acidified potassium iodide solution containing starch, gave some blue coloration, also indicating the presence of an oxidizing agent.

3.7.2. To attempt some isolation of the possible constituents of the mixture, a separation by paper chromatography was attempted, but no separate zones due to benzil or benzoin could be detected. A sensitive chemical test for benzil consisted of treating some of the solid product with one pellet of potassium hydroxide and a few drops of absolute alcohol and warming in a porcelain dish: after heating, the remains of the potassium hydroxide pellet

were removed and a few drops of concentrated sulphuric acid added. A pink or red coloration is given in this test by traces of benzil, due to the formation of benzilic acid, but no such colour was found from our samples. Benzoin also gives this reaction, and the negative result appeared to exclude the presence of both benzil and benzoin.

3.7.3. Benzoin gives a very sensitive fluorescent reaction with solutions of sodium borate in alcohol solution, with a sodium hydroxide buffer at pH 12, or in formamide solution with isobutyl amine as the base. It also reacts with solutions of sodium silicate, to give a fluorescence in the presence of sodium hydroxide and mannitol. Negative results were obtained from these reactions, but the failure could have been due to the presence of the oxidizing agent, which could easily quench the fluorescent reaction.

3.7.4. It was concluded that only dibenzoyl peroxide could be identified as a possible constituent of the irradiation products, apart from benzoic acid.

3.8. Determination of perbenzoic acid.

3.8.1. To obtain some idea of the variation of the perbenzoic acid concentration during the oxidation reaction, we can refer back to the electrometric titration experiments described in Final Report 1962, Sects. 3.3.7. and 3.5. Fig. 4, reproduced from this report, shows a set of typical electrometric titration curves for samples with various irradiation times. The two points of inflection show the presence of two acidic species, one of which decreases in concentration as the irradiation proceeds, and has virtually disappeared in 50 minutes. The known data on the benzaldehyde oxidation suggest that the unstable acid is in fact perbenzoic acid.

3.8.2. Fig. 5. shows the change of concentration of perbenzoic acid, starting 3 minutes after the commencement of irradiation, computed from several sets of titration curves. The concentrations are expressed as a percentage of the maximum possible theoretical value.

4.0 EXPERIMENTAL DETAILS: PHYSICAL

4.1. Contact potential tests

4.1.1. Apparatus The apparatus used in the first part of this program was the same as that described in Final Report 1962, Sect. 4.9.1. The electrode assembly is shown in Fig. 6, and consisted of a platinum reference electrode, supported by a large insulator, and an adjustable brass platform to support the semiconductor sample, the whole assembly being mounted on a metal base-plate and enclosed in a screening cover. The platinum electrode was about 2 cm^2 in area, and made from expanded mesh, fixed to a platinum wire frame. The amplifier used to detect the potentials was fully described in Final Report 1962 Sect. 4.9.1, and the circuit diagram is reproduced in Fig. 7. Later, a commercial amplifier, the E.I.L. Vibron Electrometer, Model 33C with A33C probe unit was used. This instrument had the advantage of giving direct readings of voltage and polarity with a high input resistance of about 10^{16} ohms (compared with 10^{11} ohms in the original apparatus). However, the readings were limited to a maximum of 1 volt and for higher values, a backing-off circuit had once again to be employed. Another electrode assembly was used in conjunction with the E.I.L. Model 33C, to provide a finer control of the electrode spacing. The assembly is shown in Fig. 8, and was designed to mount directly on the top of the A33C external probe unit of the Model 33C. In this way, stray capacitance and pick-up from connecting leads was eliminated. The germanium was mounted at the "hot" terminal of the probe, on a ball joint, to allow the top surface of the crystal to be made exactly parallel to the reference electrode. The reference electrode, a gold-plated or rhodium-plated brass disc, was at earth potential and mounted on a fine screw to allow very accurate control of the electrode spacing. The Model 33C had the disadvantages, in addition to the low maximum voltage reading, of a fairly high input capacitance of 30 pf., and a rather slow response time of up to 30 seconds. Towards the end of the program, a Wayne-Kerr Precision Electrometer M.141 was used for measurements: this instrument had the advantages of a similar high input impedance of 10^{16} ohms, low input capacitance of 3 pf, a fast response time of 1 to 2 seconds and a maximum reading of 10 volts (or up to 1000 volts with a multiplier probe of increased input capacitance of 100 pf). The M.141 could be used in conjunction with a "Hi-Speed" Chart recorder (made by Control Instruments Ltd., Barkehead, England) to give direct recordings of the growth and decay of potentials.

4.1.2. Procedure

A block of single crystal material was cut with two reasonably parallel faces, which were then smoothed with

250 mesh, followed by 600 mesh carborundum. One surface was copper-plated, to provide a base contact, while the opposite surface was etched in a variety of etching mixtures, as required. In some experiments, a ground surface was used as a base contact, and no undesirable effects could be attributed to this method. Soldered base contacts to a flying lead were employed in the previous work, described in Final Report 1962, Sect. 4.9.2, but these made the mounting of samples more difficult and were abandoned early in the present series of experiments: no significant differences were detected in the results obtained with or without the soldered contacts. The spacing between the reference electrode and the crystal surface was usually made as close as possible, and was adjusted to about 0.2 mm. The whole electrode assembly was enclosed in the metal screening cover, to exclude stray electrostatic fields, although in the laboratory-constructed equipment it was not possible to obtain complete screening, as about 10 cm. of connecting wire was used between the electrode and the amplifier. With the E.I.L. Model 33C, the electrode assembly was built on to the probe and with the Wayne-Kerr M.141, a short piece of special screened lead was used for connection to a coaxial plug; in these cases almost complete screening was obtained. The space around the electrode assembly was flushed with dry oxygen at a flow rate of about 1.5 litres per minute, and the measuring equipment was switched on to attain a stable working condition. Moisture was introduced as required by switching the gas stream through a water bubbler: this introduced approximately 0.015 g. H_2O per litre of gas. Chart recordings of the variation of potential with time were made by coupling a Hi-Speed potentiometric recorder (manufactured by Control Instruments) to the Wayne-Kerr M.141

4.2. Confirmatory experiments on earlier potential measurements

4.2.1. In view of the unusually high values obtained in the earlier contact potential measurements, detailed in Final Report 1962, Sect. 4.10, it was decided to carry out a series of similar measurements with the same equipment for confirmatory purposes. These measurements were not so detailed as the earlier series and were designed only to confirm the high voltages obtainable and to look for any spurious effects which might give rise to such values.

4.2.2. The platinum reference electrode was set to a spacing of about 0.2 mm. in each case, as this had previously been found to be a suitable value. A fresh surface was prepared on the germanium crystal for each experiment by treating with CPI etch. In dry oxygen, apparent contact potentials of between 0 and 80 mV were recorded, but it should be remembered that this value included an internal contact potential of about 30 mV from the apparatus, which probably varied from time to time.

Such variations were of no significance in determining the validity of potentials in the 10 to 100 volt range.

4.2.3. To test the possibility that the results obtained might be affected by the presence of foreign matter, (e.g. fibres) on the surface of the platinum mesh, the platinum was heated to a bright red heat in a bunsen burner before being used for this series of experiments. This treatment would have burned away any organic fibres and volatilized many possible adsorbed chemical compounds. The platinum was subsequently handled with great care, using tweezers only, and kept always under cover, to prevent any deposition of dust or fibres.

4.2.4. The potentials obtained in this series of experiments were more unpredictable than those in the earlier experiments, and for some time no potentials higher than about 2 V were recorded. Later, maximum readings of 32 volts and 15.5 volts were recorded on two consecutive runs. The appearance of these potentials could not be correlated in any way with the surface preparation of the sample, the experimental conditions or any defects in the measuring equipment.

4.2.5. The lack of success in obtaining high potentials was at one stage suspected to be the result of having heated the platinum to a high temperature. It is well known that hydrogen, if adsorbed in atomic form, may lower the work function of platinum by 2 volts or more (19) and it has been found that the correct value of 6.3 volts is only obtainable after very careful out-gassing (20). The platinum electrode was therefore cathodically reduced in dilute sulphuric acid at a current of 3A for some time, and carefully washed and dried before continuing with the experiments. No immediate increase in the potentials obtained was noted, but after several runs had been carried out, the high values of 32 volts, and 15.5 volts were found on two consecutive occasions. This success could not be repeated, however, and no effect of the exposure of the crystal surface to an irradiated film of benzaldehyde could be demonstrated. The effect of ammonia gas was investigated in one experiment by bubbling the oxygen through 0.880 ammonia solution. The figures obtained in some of these experiments are tabulated below. All voltages were measured by the null method on a potentiometer, and were always found to be positive. A blank test, using a brass block instead of the germanium sample, in wet oxygen gave a constant reading of only about 20 mV.

4.2.6. Contact potential readings, (1.1.1.) surface of
4 ohm.cm n-type Ge
Electrode spacing 0.2 mm

<u>Expt</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Time</u> <u>mins</u>	<u>Voltage</u> <u>+</u>	<u>Remarks</u>
1	1	Perborate etch	0	0.08	Dry O ₂
			4	1.0	Wet O ₂
			10	0.9	
	2	Left for 60 mins in dry atmosphere	0	0.08	Dry O ₂
			1	0.8	
			2	1.6	
			3	1.9	
			4	1.85	
			5	1.8	
			8	1.7	
			9	1.6	
			11	1.5	
			15	1.4	
			17	1.2	
			21	1.1	
			25	1.0	
			32	0.9	
			39	0.8	
			56	0.7	
			93	0.63	Dry O ₂
			93.5	0.08	
			95	0.08	Wet O ₂
			98	0.5	
			99	0.55	
			101	0.58	
			103	0.59	
			108	0.61	
			116	0.65	
	3	Left for 16 hrs in dry atmosphere	0	0.04	Dry O ₂
			1	0.6	
			1.5	1.2	
			2	1.6	
			3	1.8	
			4	1.8	
			5	1.7	
			6	1.6	
			7	1.6	
			9	1.5	
			11	1.3	
			13	1.2	
			16	1.1	
			19	1.0	
			21	0.9	
			23	0.8	

<u>Expt</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Time</u> <u>Mins</u>	<u>Voltage</u> <u>+</u>	<u>Remarks</u>
1	3		29	0.7	
			34	0.6	
			44	0.5	
			63	0.4	
			111	0.35	
			171	0.33	Dry O ₂
			172	0.04	
2	1	Benzaldehyde + U.V. Light for 10 minutes	0	0.03	Dry O ₂
			2	0.5	Wet O ₂
			3	0.5	
			7	0.4	
			14	0.3	
3	1	Re-etched in CPI	0	0.01	Dry O ₂
			1.5	0.7	Wet O ₂
			2.5	1.0	
			4	1.15	
			5	1.1	
			6	1.1	
			8	1.0	
			11	0.7	
			13	0.6	
			16	0.5	
			20	0.4	
			24	0.35	
			30	0.3	
			60	0.27	
			80	0.25	Dry O ₂
			81	0.07	
	2	Pt-electrode cathodically reduced at 3A in H ₂ SO ₄ soln.	0	0.035	Dry O ₂
			1	0.8	Wet O ₂
			2	1.2	
			3	1.7	
			6	2.1	
			7	2.3	
			9	2.5	
			12	1.5	
			15	1.4	
			17	1.3	
			23	1.2	
			28	1.1	
			31	1.0	
			32	1.0	Dry O ₂
			34	0.045	
			37	0.045	Wet O ₂
			38	0.2	
			42	0.045	

<u>Expt</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Time</u> <u>Mins</u>	<u>Voltage</u> <u>+</u>	<u>Remarks</u>
3	3	Left for 3 hrs in dry atmosphere	0	0.01	Dry O ₂
			1	0.5	Wet O ₂
			2	0.6	
			3	0.7	
			7	0.8	
			9	0.7	
			11	0.6	
			13	0.5	
4	1	Benzaldehyde + U.V. light for 10 minutes	0	0.0	Dry O ₂
			3	0.2	Wet O ₂
			4	0.3	
			5	0.4	
			7	0.5	
			9	0.65	
			11	0.65	
			13	0.7	
			18	0.65	
			22	0.65	
5	1	Re-etched in CPI	0	0.01	Dry O ₂
			2	0.06	O ₂ through
			12	0.06	0.880 NH ₃ solution?
			13	0.01	Dry O ₂
			23	0.01	
			24	0.3	Wet O ₂
			30	32.0	
			35	32.0	
			41	30.0	
			48	24.3	
			51	22.5	
			59	16.8	
			63	15.0	
			74	12.0	
	2	Left for 16 hrs. in dry atmosphere	0	0.0	Dry O ₂
			0.5	0.1	Wet O ₂
			1.5	9.3	
			4	15.0	
			7	15.5	
			8	15.0	
			14	9.3	
			18	7.5	
			20	6.0	
			26	4.5	
			39	3.0	

<u>Expt.</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Time</u> <u>Mins</u>	<u>Voltage</u> <u>+</u>	<u>Remarks</u>
6	1	Benzaldehyde + U.V. light for 10 minutes	0	0.0	Dry O ₂
			2	0.02	Wet O ₂
			5	0.02	
			10	0.02	
	2	Left for 50 mins in dry atmosphere	0	0.0	Dry O ₂
			1	0.4	Wet O ₂
			2	1.0	
			2.5	1.5	
			3	1.8	
			4	2.0	
			5	2.1	
			8	2.4	
			12	2.3	
			14	2.3	
			16	2.2	
			17	0.02	Dry O ₂
			46	0.01	
			50	0.02	O ₂ through
			55	0.02	0.880
					NH ₃ solution
			59	0.01	Dry O ₂
	3	Left for 2½ hrs. in dry atmosphere	0	0.0	Dry O ₂
			1	0.4	Wet O ₂
			3	2.9	
			4	4.7	
			7	5.5	
			9	5.5	
			12	5.3	
			16	5.1	
7	1	Re-etched in CPI Pt-electrode anodically oxidized at 3A in H ₂ SO ₄ soln.	0	0.01	Dry O ₂
			1	1.7	Wet O ₂
			5	1.5	
			10	0	
8	1	Re-etched in CPI	0	0.0	Dry O ₂
			1	0.0	Wet O ₂
			5	0.01	
			10	0.01	
	2	Pt-electrode cathodi- cally reduced at 3A in H ₂ SO ₄	0	0.0	Dry O ₂
			1	0.0	Wet O ₂
			6	0.0	
			10	0.01	
	3	Pt and Ge exposed to NH ₃ before test	0	0.0	Dry O ₂
			2	0.01	Wet O ₂
			15	0.01	

4.3 Potential measurements with the E.I.L. Model 33C

4.3.1. The experiments described in the foregoing section demonstrated the non-reproducible nature of the results obtainable with the existing apparatus. A direct-reading commercial instrument, the E.I.L. Model 33C was, therefore, obtained and further measurements were carried out.

4.3.2. The new electrode assembly shown in Fig. 5 was used, and fixed directly to the A33C external probe unit: with this system there was very little stray capacity and all the electrodes and connections were completely screened. Two windows, cut in the wall of the apparatus allowed easy access to the electrodes: during the measurements, these windows were blocked by a sliding brass collar, thus completing the earthed screen around the whole assembly.

4.3.3. The first step was to establish the relation between the readings obtainable on the old apparatus and the readings on the E.I.L. Model 33C. A series of measurements was carried out with the electrode assembly, containing a germanium sample, connected to both sets of measuring equipment. It was shown that there was some interaction between the two and the E.I.L. instrument did not respond correctly to increments of the backing-off voltage, applied to the first instrument by a potentiometer. However, when the backing-off voltage was adjusted to give a zero reading on both instruments, the potentiometer reading agreed very well, in every instance, with the direct reading of the E.I.L. Model 33C, when used alone. Thus there was no serious disagreement in the values given by the two instruments.

4.3.4. The backing-off circuit was the parallel type, used originally, and illustrated in Fig. 9. We also tried the classical, series backing-off circuit, as shown in Fig. 10, and found this to give satisfactory results, although it had proved unsatisfactory in our early experiments. The response time of the series backing-off circuit when used with the E.I.L. Model 33C, was in the region of 1 or 2 minutes, so that the measurement of transients, or even slow changes in potential taking a few seconds, was impossible for potentials in excess of 1 volt. For the direct reading of potential up to 1 volt, the response time was 20 to 30 seconds. A comparison of the merits and sources of error of the backing-off circuits is discussed later in Sect. 6.4. A sample of 4 ohm-cm., n-type, (1.1.1) crystal was used for these tests.

4.3.5. A large number of potential measurements of the Ge/ambient/Au and Ge/ambient/Rh system were made using the normal dry and wet oxygen cycle. A considerable amount of care was taken to ensure that the germanium and reference electrode surfaces were free from any contamination, and the electrode spacing was carefully adjusted to the region of 0.1 to 0.2 mm.

4.3.6. To determine whether high potentials were associated with a particular type of surface preparation, a wider range of surface treatments was investigated. These were:

- (1) Ground surface with 600 mesh carborundum.
- (2) Chemical polish, using CPI or CP4A etch.
(CP4A etch is made from 3 parts HF + 5 parts HNO_3 + 3 parts H.Ac.)
- (3) Dislocation etching, using W.Ag etch
(W.Ag etch is made from 2 parts HF + 1 part HNO_3 + 2 parts 5% AgNO_3 soln).
- (4) Anodic polarization in 10% H_2SO_4 , HCl or HF solutions.
- (5) Anodic polarization in 10% NaOH .
- (6) Cathodic polarization in 10% H_2SO_4 , HCl or HF solutions.
- (7) Cathodic polarization in 10% NaOH .

4.3.7. In other experiments, the specimen, after the chemical surface preparation, was placed for long periods in a vacuum at 10^{-5} to 10^{-6} mm. Hg pressure, before being tested. In some cases the specimen was heated to about 150°C during vacuum treatment, by an infra-red lamp, to help drive off adsorbed volatile compounds, particularly water.

4.3.8. The potentials obtained in this series of experiments tended to be very variable and non-reproducible and were usually in the range 30-100 mV. There was some evidence to suggest that more than one potential gradient was present: if the electrode system was allowed to reach a steady state, for a particular spacing, it was found that decreasing the spacing rapidly would then cause the potential to decrease and actually reverse polarity. No significant difference was observed between any of the many treatments described in the previous two paragraphs.

4.3.9. The introduction of a drop of distilled water between the germanium surface and the reference electrode was found to give a immediate potential of about 500 mV, and this potential was rapidly and reproducibly regenerated after momentarily short-circuiting the electrodes. Potentials in this region had been obtained at infrequent intervals throughout the series of experiments, but could not be correlated with surface treatment or the experimental conditions. The voltage developed across the water drop was independent of the cross-sectional area, suggesting a possibility that potentials of the order of 500 mV might have been provided by the bridging of the

electrode gap by minute whiskers or dust particles. Some tests were carried out, introducing a few filter paper fibres in the 0.2 mm. gap between the electrodes, and measuring the potential obtained in wet oxygen; readings of about 500 mV were obtained in every case. The rate of recovery of the potential after short circuiting the electrodes varied considerably, and appeared to depend on the conductivity of the fibres: typical recovery times were 5 to 30 seconds.

4.3.10. During the whole series of experiments there was only one example of a high potential being recorded. On this occasion, both the old and the new measuring equipment were connected together and without any backing-off potential the E.I.L. Model 33C was reading off-scale at + 1 volt. Application of the backing-off potential from the potentiometer system enabled both instruments to be brought to zero, when it was noted that the required potential was -30 volts. The usual short-circuit tests were carried out to make sure that there was no charge accumulation on the electrode, and the potential returned to the high value each time. The voltage gradually decayed with time in the same manner we had observed frequently in the earlier work.

4.4. Potential measurements with the Wayne-Kerr M.141

4.4.1. Measurements were continued with the Wayne-Kerr M.141 Precision Electrometer, in the hope of making direct readings of potentials greater than 1 volt and of detecting any voltage transients, which could be observed on an instrument with a response time of about 1 second. The original electrode assembly (Fig. 6) was used, connected to the Wayne-Kerr by a short length of special non-static co-axial cable: the cable screening was connected to the guard terminal of the instrument, so that it contributed little to the input capacitance.

4.4.2. A series of measurements on a 2.5 ohm-cm n-type crystal was carried out in the usual way in dry and wet oxygen, for the Ge/ambient/Pt system, generally using perborate or CPI etches for surface preparation. Variable potentials between about +50 and +500 mV were usually obtained. However, there were occasional exceptions to this rule. In one experiment, a consistent +530 mV. was obtained, recovering rapidly each time the electrodes were short-circuited. The electrode gap of 0.3 mm. was examined very carefully with a lens, using strong background illumination, but no trace of microscopic fibres in the gap could be seen. In another experiment, a high voltage, in excess of 10 volts, developed about 1 minute after the introduction of wet oxygen to the apparatus. Unfortunately, the X100 probe was not connected at this time and the exact value of the voltage could not be obtained. The electrodes were short-circuited several times, to remove any stored charge, but the potential returned rapidly to over 10 volts. The

voltage had decayed below 10 volts in about 10 minutes and was clearly following the familiar decay curve obtained in earlier experiments. This sample was allowed to stand for 90 minutes in dry air, inside the screening cover, and then a further treatment with wet oxygen was given, this time with the X 100 probe connected to the meter: no repetition of the high voltage could be obtained, however. A close examination of the electrode system with a lens showed a very small fibre attached to the platinum, but apparently not bridging the gap; this may have had no connection with the results obtained.

4.4.3. Among the special tests carried out in this series were the introduction of cotton fibres into the electrode gap and the separation of the electrodes by a 1 mil. polythene film: measurements were also made in oxygen containing ammonia, diethyl ether or methanol vapours. The measurements in the presence of cotton fibres gave fairly consistent readings in wet oxygen of between 500 and 600 mV: the introduction of ammonia raised the potential to the 700 to 800 mV region, while diethyl ether and methanol gave much lower values. The voltages obtained with the polythene film spacer were very variable and both positive and negative potentials were obtained, probably due to a combination of resistive and capacitive effects. The electrodes and the polythene were only loosely in contact, and there was ample space for the diffusion of water vapour to the surface of the crystal. The figures obtained in all these measurements are detailed in the table below.

4.4.4. Potential readings (1.1.1) surface of 2.5 ohm-cm-n-type Ge, Electrode spacing 0.2 mm (unless otherwise stated)

<u>Expt</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Max.</u> <u>Voltage</u> +	<u>Remarks</u>
1	1	Pt. electrode cathodically reduced at 3A in H_2SO_4 soln		Load resistor 2.5×10^{10} ohms. Electrode spacing 0.3 mm.
		Ge ground on 600 mesh carborundum, etched in perborate.	0.050	Dry O_2
			0.530	Wet O_2
	2	5 mins. in dry O_2	0.050	Dry O_2
			0.510	Wet O_2
				Electrode gap examined for fibres, but none detected.

<u>Expt.</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Max.</u> <u>Voltage</u> <u>+</u>	<u>Remarks</u>
	3	10 mins. in dry air	0.015 0.055 0.057	Dry air Dry O ₂ Wet O ₂
	4	40 mins. in dry air Pt-electrode cathodi- cally reduced at 3A in H ₂ SO ₄ soln. for 30 mins.	0.033 0.110 0.130	Dry air Dry O ₂ Wet O ₂ . Voltage fell rapidly
2	1	Re-etched in CPI Baked on hot-plate at 150°C for 3 mins.	0.070 0.130	Dry O ₂ Wet O ₂
3	1	Re-ground on 30 $\frac{1}{2}$ Aloxite Etched in perborate	0.080 0.150	Dry O ₂ Wet O ₂ Voltage fell rapidly
	2	Baked on a hot plate at 200°C for 5 mins	0.080 0.030	Dry O ₂ Wet O ₂ . Falling to 0.015 ²
4	1	Re-etched in perborate + ammonia.	0.070 0.110	Dry O ₂ Wet O ₂ . Voltage fell rapidly
	2	Left for 2 days in dry atmosphere	0.070 0.060	Dry O ₂ Wet O ₂

<u>Expt.</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Max.</u> <u>Voltage</u> +	<u>Remarks</u>
5	1	Re-etched in CPI	0.040	Dry O ₂
			0.300	Wet O ₂
	2	Left for 20 mins in dry air	0.040	Dry air
			0.100	Dry O ₂
			0.360	Wet O ₂
6	1	Benzaldehyde + U.V. Light for 10 mins.	0.095	Dry O ₂
			0.120	Wet O ₂
7	1	Ground on 280 mesh carborundum, cleaned with water and soap, but not etched.	0.010	Dry air
			0.030	Dry O ₂ Rising to 0.060 in 5 mins.
			0.090	Wet O ₂
8	1	Etched in perborate	0.050	Dry O ₂
			-0.010	Wet O ₂
9	1	Re-ground on 600 mesh carborundum and 303 $\frac{1}{2}$ Aloxite. Etched in perborate	0.040	Dry O ₂
			0.110	Wet O ₂
	2	Left for 20 mins. in dry air	0.090	Dry O ₂
			0.100	Wet O ₂
10	1	Re-etched in CPI	0.030	Dry O ₂
			0.180	Wet O ₂
11	1	Re-etched in W-Ag	0.045	Dry O ₂
			0.080	Wet O ₂
	2	Ge exposed to NH ₃ vapour before test.	0.070	Dry O ₂
			0.080	Wet O ₂
12	1	Re-etched in CPI Cotton fibres placed in electrode gap	0.030	Dry O ₂
			0.520	Wet O ₂

<u>Expt.</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Max.</u> <u>Voltage</u> +	<u>Remarks</u>
13	1	Re-ground on 600 mesh carborundum. Etched in perborate. Cotton fibres placed in electrode gap	0.030 0.550	Dry O ₂ Wet O ₂
14	1	Re-etched in NaOCl + NaOH. Cotton fibres placed in electrode gap.	0.035 0.580	Dry O ₂ Wet O ₂
	2	Left for 20 mins. in dry air Oxygen bubbled through 0.880 NH ₃ soln.	0.035 0.700	Dry O ₂ Wet O ₂ + NH ₃
	3	Left for 5 mins. in dry O ₂ flow.	0.035 0.800	Dry O ₂ Wet O ₂ + NH ₃
	4	Left for 10 mins. in dry O ₂ flow. Oxygen bubbled through Et.O.Et	0.300	O ₂ + EtOEt
	5	Left for 10 mins. in dry O ₂ flow. Oxygen bubbled through MeOH	0.200	O ₂ + MeOH
15	1	Re-etched in CPI Pt electrode separated from Ge by 1 mil. polythene film	+0.600 -0.100 +0.250	Dry air Dry O ₂ Wet O ₂ . Falling to +0.020 in 20 mins.
16	1	Surface ground on 600 mesh carborundum Not etched. Pt. electrode separated from Ge by 1 mil polythene film.	+0.150 -0.130 +0.510	Dry Air Dry O ₂ Wet O ₂

<u>Expt.</u> <u>No.</u>	<u>Run</u> <u>No.</u>	<u>Treatment of surface</u>	<u>Max.</u> <u>Voltage</u> +	<u>Remarks</u>
17	1	Re-etched in CPI Pt electrode separated from Ge by 1 mil. polythene film.	+0.340 -0.200 -0.230	Dry air Dry O ₂ Wet O ₂ Comm- encing at -0.100
18	1	Re-etched in NaOCl-NaOH soln. Pt. electrode separated from Ge by 1 mil. poly- thene film.	+0.270 -0.190 -0.540	Dry air Dry O ₂ Wet O ₂ - commen- cing at + 0.050
	2	Benzaldehyde + U.V. Light for 10 mins	+0.100 -0.180 -0.300	Dry air Dry O ₂ Wet O ₂ - commencing at -0.100

4.5 Potential readings with continuous recording from the Wayne-Kerr M.141 and using a glass fibre probe.

4.5.1. The next series of experiments was conducted to determine the time-voltage characteristic of the surface potential under changing conditions of ambient, and after disturbing the electrical equilibrium of the system.

4.5.2. The output of the Wayne-Kerr M.141 was connected to the Hi-Speed potentiometric recorder (full scale 5 mV) by a potential divider: a 330 ohm and a 10 ohm resistor were connected in series across the output, and the recorder was fed across the 10 ohms.

4.5.3. At this stage in the investigation, it had been decided that some form of conducting path to the surface of the sample from the platinum was probably essential to give meaningful readings on the state of the surface. In view of the very high input resistance of the measuring equipment (10^{16} ohms possible maximum, but about 10^{15} ohms in this particular practical application), the use of glass fibre as a probe material seemed to be very suitable. A number of fibres were cemented to the platinum grid so that they would contact the surface of the germanium sample at a distance of 1 to 2 mm. For a typical germanium sample, it was found that the path from platinum to germanium had a resistance of about 10^{10} ohms; this was sufficiently low compared with the input resistance to give a negligible voltage drop. The time constant of the system, assuming an input capacitance of 3 pf., was then only 0.03 sec., much shorter than that of the instrument itself (1 second), so that there was a negligible effect on the response speed.

4.5.4. It was hoped that the glass fibres would be able to probe the surface potential of the sample without disturbing the system either electrically or mechanically. While conduction probably takes place in the surface layer, it is not necessary to assume this in interpreting the readings; for a sample with reasonably uniform surface properties, the average potential picked up from a number of isolated areas by the various fibres should be equally acceptable.

4.5.5. In the sequence of experiments three types of germanium were examined, viz. n-type, p-type, near-intrinsic. The samples were etched with CPT reagent, mixed with distilled water and then examined in the wet and dry ambients. After the first cycle of voltage recordings the specimen was removed and anodised in 20% ammonium acetate solution for 10 minutes at 50 mA.cm^{-2} . The specimen was then rinsed and re-cycled as before. The ambient was either dry oxygen or oxygen bubbled through distilled water.

4.5.6. At the commencement of a run, moist oxygen was passed through the electrode chamber and the voltage of the system allowed to reach a fairly steady value. This value varied from 300 to 700 mV but was most frequently found to be about 500 mV, the germanium being negative to the platinum. Next, the ambient was changed to dry oxygen by simply by-passing the bubbler, whereupon the voltage commenced to decay to about zero. The voltage was then regenerated by returning to a moist oxygen ambient. Upon reaching a steady value the electrodes were momentarily short-circuited after which the potential rose rapidly to its steady value. The reverse effect, i.e. the momentary application of an external field slightly in excess of the steady voltage, was also examined. The ambient was then changed to dry oxygen and a second recording of the decay obtained. Finally, when this voltage had reached a minimum, the external field was momentarily applied for a second time and the resulting decay curve recorded. A few variations to this scheme were also tried and they will be mentioned in the discussion.

4.5.7. Results

Some of the actual curves obtained are illustrated in Figs. 21-23. However, since no radical difference in behaviour was noted between any of the specimens, the general form of the results is illustrated by the idealized curve given in Fig. 20. A detailed interpretation of these results will be given in Sect.6.4.

4.6 Measurement of surface recombination rate by the Photoelectromagnetic effect

4.6.1 Apparatus. The prepared germanium sample was mounted in the gap of a reasonably powerful permanent magnet (1100 gauss). Illumination was provided by a 300 watt projector lamp, through a lens system of 10 cm. diameter and a water cell 2.5 cm. deep, to absorb heat radiation. The open-circuit output voltage from the specimen was measured accurately by a backing-off potentiometer in series with a sensitive null indicator of high impedance. The original contact potential amplifier, shown in Fig. 7, was used as the null indicator: the very high input impedance was useful in providing a sharp balance point. A diagram of the whole assembly is given in Fig.11.

4.6.2. Procedure. Slices of germanium were cut from a 40 ohm-cm n-type crystal, with a minority carrier lifetime of about 200 microseconds. The samples were about 0.8 mm. thick, 2 cm. long and 1 cm. wide, and the surfaces were prepared by grinding on 280 mesh followed by 600 mesh carborundum: the thickness was accurately measured with a micrometer. The surfaces were then electroless-copper plated in a CuSO_4/HF mixture, as described by Davies and Milne (21). 100 ml. of saturated aqueous copper sulphate solution was mixed with 4 ml. 40% hydrofluoric acid solution and the ground sample was immersed in the solution for 5 to 10 minutes.

Two small spots of wax were placed on one side of the sample, about 1.5 cm. apart, where the probe contacts were required, and the whole sample was immersed in 50% nitric acid for a short while to remove the excess copper. The sample was then washed in double-distilled water, followed by benzene to remove the spots of wax. This provided two small copper spots for attachment of the probes. The copper was tinned by gradually heating the sample on a hot plate to about 250°C . and touching with a small piece of resin-cored solder. After cooling, fine leads could be attached to the solder, using a finely pointed soldering iron. The short lengths of fine wire were supported by heavier leads of 20 gauge wire, which formed the external connections.

The sample was supported in a horizontal position about 8 mm. above a microscope slide with the connecting leads extended on either side. A cylindrical polythene former was placed around the assembly, to act as a mould, and Araldite was poured in, just to the level of the upper germanium surface. The assembly was baked at about 100°C . for 2 hours to cure the resin, after which the polythene mould could be peeled away. The projecting ends of the glass slide can be cut away, if required. A section of a mounted sample is shown in Fig.12. The thickness of the whole assembly was then accurately checked with a micrometer and compared with the slice thickness,

as previously recorded, so that a check could be kept of the sample thickness during subsequent experiments. The surface of the sample was lightly re-ground on 600 mesh carborundum then etched 3 times in small quantities of CPI etch, to give a clean polished surface, washed well in double-distilled water and dried. The sample was then ready for use. It was mounted, as shown in Fig.11, with the line joining the two probe contacts perpendicular to the magnetic field. The lamp was adjusted to focus the maximum amount of light on the sample; this is best carried out by adjusting for a maximum output voltage. Any residual potentials were first balanced out on the potentiometer then the output voltage with illumination was measured. Only short periods of illumination were used, to avoid thermal effects. In each experiment the surface was treated as required, measurements taken and compared with standard readings, to obtain an estimate of the effect of the surface treatment on surface recombination rate.

4.6.3. Principles of the method. The photoelectric-magnetic effect (PEM) is a variation of the Hall effect in which carriers are optically generated, and by interaction with the magnetic field generate a current or voltage in the specimen. A simplified diagram is given in Fig.13, which illustrates the creation of a hole-electron pairs by the adsorption of a photon at the upper surface of the crystal. The hole-electron pair drifts a diffusion length L into the crystal, and is separated by the transverse magnetic field B into a separate hole and electron, spaced at the Hall angle θ . In short-circuit conditions, one pair per second will contribute one unit of current in the lateral direction if the charges are separated by the length of the sample: in practice, the splitting is much less and the contribution of the injected carriers will be reduced by the factor $\theta (L/l)$, where l is the length of the sample. When F photons/sec. are absorbed, the total short circuit current will be

$$I_s = Fe \theta (L/l)$$

As shown by Shockley (22) we can substitute

$$\theta = \mu B$$

$$L = (\mu \tau kT/e)^{\frac{1}{2}},$$

where μ and τ are the effective mobility and lifetime respectively and kT/e is the temperature in electron volts. The relation then becomes,

$$I_s = Fe \mu B \frac{(\mu \tau kT/e)^{\frac{1}{2}}}{1}$$

$$\text{or } I_s = \frac{FeB (kT/e)^{\frac{1}{2}} (\mu^3 \tau)^{\frac{1}{2}}}{1}$$

The open-circuit voltage $V = RI_s$, for a sample of resistance R . Thus, the short circuit current is proportional to the light flux per unit length of crystal, F/l , to the magnetic field B and to $(\mu\tau)^{1/2}$. For exact calculations, the differences between Hall and diffusion mobilities must be allowed for, and the single mobility giving the best approximation is probably the majority carrier mobility: the minority carrier lifetime is the best figure to use for the effective diffusion lifetime L .

Similar relations have been derived by Moss ⁽²³⁾ and by Aigrain ⁽²⁴⁾. The equations have been extended to include surface recombination velocity by Pincherle ⁽²⁵⁾ and by Kurnick and Zitter ⁽²⁶⁾ and the most complete treatment has been given by van Roosbroeck ⁽²⁷⁾. Applications of the PEM method to the measurement of surface recombination velocity have also been discussed by Moss et al. ⁽²⁸⁾, Bulliard ⁽²⁹⁾, Hilsum et al. ⁽³⁰⁾ and Hall ⁽³¹⁾. The mathematical analysis has shown that when the intensity of illumination is high, at about 10^{18} photons/cm²/sec. the equation involving the surface recombination velocity S approximates to the form,

$$V = 10^{-8} . lBS$$

where V is measured in volts

l is the distance between the contacts in cm.
 B is the field in gauss.
 S is in cm./sec.

The factor 10^{-8} is present as a consequence of the units employed. For accurate PME measurements of S , the van Roosbroeck ⁽²⁷⁾⁽³²⁾ method requires S to be determined on the dark surface of the specimen. The short circuit PME current is measured and also the relative conductance increase at the same light intensity, but with no magnetic field. The ratio of these quantities, multiplied by a factor containing constants for the material, is used to calculate S . The use of relative conductance increase avoids the necessity of determining the light intensity or S at the illuminated surface exactly. The maximum output obtainable for a given specimen depends to some extent on resistivity, volume lifetime, recombination at both surfaces, light intensity and specimen thickness, all of which should be taken into consideration.

However, for the determination of approximate values and making comparative measurements, the simplified relation derived by Moss, Pincherle and Woodward ⁽²⁸⁾ i.e. $V = 10^{-8} lBS$, was considered to be suitable. Our practical experiments were based on the work of Buck and Brattain ⁽¹⁴⁾ and Buck and McKim ⁽¹⁵⁾, who used the simplified system for comparing the effects of surface treatments and for determining the depth of abrasion surface damage. Referring now to Fig.12,

if the illuminated surface L is initially etched, to give a low recombination rate, and the dark surface D is ground to give a very high recombination rate, then a maximum output on illumination will be obtained: progressive etching of the dark surface would cause the output to fall and tend towards a very small constant value. Similarly if both L and D are initially ground to give high recombination rates, then a very low output on illumination will be obtained: progressive etching of the illuminated surface L would cause the output to increase and tend towards a constant maximum value. This reciprocal behaviour is illustrated in Fig.14, which is based on the results of Buck and Brattain (14).

There are certain disadvantages in studying the effects of surface treatment on the dark surface, as it is useful to set this region in a hard plastic to protect the fine contacts from damage, and there may be some contamination of the surface from these contacts during chemical treatment. In our experiments we were interested in observing any effect of benzaldehyde and irradiation on the surface recombination rate at an etched surface, and it was clearly more convenient to do this at the exposed, illuminated surface. The reciprocal relation of the two curves in Fig.14 show that one can legitimately make the experiments using either of the two surfaces. If the thickness of the sample is small compared with the diffusion length of the injected carriers, the surfaces can be regarded as almost coincident. In either case, great accuracy cannot be obtained, as the maximum or minimum values of V are approached asymptotically as the test surface approaches a well etched condition, and it is necessary to assume (from published data) some representative value for S for an etched or a ground surface before any calculations can be made.

The results of Buck and Brattain (14) suggest that a further approximate relation can be derived from the simplified equation, involving values of S for both surfaces. The relation is

$$V = 10^{-18} I_B (S_D - S_L)$$

where S_D is the surface recombination velocity at the dark surface D.

S_L is the surface recombination velocity at the illuminated surface L.

When $S_D = S_L$, either when both are ground or when both are etched, then $V \rightarrow 0$ and when S_D is ground and S_L is etched $V \rightarrow$ maximum. Suppose that when L receives a normal etching

treatment, with D remaining in the ground condition, with a constant high value of S, the PEM voltage is V_1 .

Then $V_1 = 10^{-8} \text{ lB } (S_D - S_{L1})$.

If L is given an additional surface treatment (e.g. by benzaldehyde) the PEM voltage is V_2 .

Then $V_2 = 10^{-8} \text{ lB } (S_D - S_{L2})$.

So $V_2 - V_1 = 10^{-8} \text{ lB } (S_{L1} - S_{L2})$

Or $dv = 10^{-8} \text{ lB} \cdot dS$

Where ds is the small change brought about by the additional treatment.

It should therefore be possible to calculate the change in the value of S for such a treatment.

For a constant magnetic field strength and constant light flux, the value of V depends on the concentration gradient across the sample. The concentration gradient is a function of the difference in recombination rates at the two surfaces, $(S_D - S_L)$. The relationship given above is therefore justified, to a first approximation.

4.6.4. Measurements of the photoelectromagnetic effect and the influence of benzaldehyde treatment

The illumination by the 300 watt projector lamp, focused on the surface of the sample, gave a light intensity of about 10^{18} quanta/cm²/sec., which was sufficient to give saturation. The magnetic field strength was 1100 gauss. Two samples were used, one commencing at 0.025 cm. thick, the other at 0.075 cm. No significant difference was noted in the average results obtained from each sample, showing that the diffusion length was considerably greater than the sample thickness. The samples were 40 ohm-cm. n-type germanium with a minority carrier lifetime of about 200 microseconds. Some indications of long term changes in S were observed, the value decreasing for about 5 minutes after etching or benzaldehyde treatment and increasing after several hours exposure to the atmosphere. The readings obtained are shown below.

Sample 1. Thickness (initial), 0.075 cm.
Electrode spacing, 1.5 cm.

<u>Expt.</u> <u>No.</u>	<u>Surface treatment</u>	<u>PEM</u> <u>voltage</u>	<u>Voltage</u> <u>change</u>	<u>Remarks</u>
1	CPI etch	0.064		
		0.077	+0.013	Left for 2 hrs.
	Treated with CuSO_4 soln.	0.075	-0.002	
2	CPI etch and treated with CuSO_4 soln.	0.065		
	Ph. CHO + U.V. light for 10 mins.	0.065	0	
		0.065	0	Left for 2 hrs.
3	CPI etch	0.065		
	Ph. CHO + U.V. light for 10 mins.	0.065	0	2 min. after treatment
		0.080	+0.015	20 min. after treatment
	Treated with CuSO_4/HF mixture	0.065	0	
		0.075	+0.010	3 hrs. after treatment
	Re-treated with CuSO_4/HF mixture	0.065	0	5 min. after treatment
	Ph. CHO + U.V. light for 10 mins.	0.070	+0.005	2 min. after treatment
		0.075	+0.010	5 min. after treatment
		0.065	0	16 hrs. after treatment
	Ph. CHO + U.V. light for 10 mins.	0.070	+0.005	5 min. after treatment.
		0.070	+0.005	3 hrs. after treatment.
	<u>Average</u>	0.069		

Sample 2. Thickness (initial) 0.025 cm.
Electrode spacing 1.3 cm.

Expt. No.	Surface treatment	PEM Voltage	Voltage change	Remarks
1	CPI etch	0.058		
	Ph.CHO + U.V. light for 10 mins.	0.061	+0.003	
2	Re-ground. Perborate etch	0.047		
	Ph.CHO + U.V. light for 10 mins.	0.051	+0.004	
	Ph.CHO + U.V. light for 10 mins.	0.045	-0.002	
3	CPI etch	0.050		
		0.070	+0.020	Left for 1 hr.
	Ph.CHO + U.V. light for 10 mins.	0.075	+0.025	
	Ph.CHO + U.V. light for 10 mins.	0.095	+0.045	1 min. after treatment.
		0.050	0	10 min. after treatment.
		0.075	+0.025	Left for 2 days
	Ph.CHO + U.V. light for 10 mins.	0.045	-0.005	1 min. after treatment.
4		0.065		
	Ph.CHO + U.V. light for 10 mins.	0.065	0	5 min. after treatment.
<u>Average</u>		0.061		

After each surface treatment the sample was washed with double-distilled water and acetone and dried.

For the purposes of comparing the behaviour of the two samples, the value for S at the ground surface will be calculated for each, using the average value of the P.E.M. voltages obtained, by means of the standard formula.

For Sample 1, the average is 0.069 V.

$$V = 10^{-8} \text{ lbs}$$

$$\text{So } 0.069 = 10^{-8} \cdot 1.5 \cdot 1100 \text{ S}$$

$$S = \frac{0.069 \cdot 10^8}{1.5 \cdot 1100} = \underline{4200 \text{ cm/sec.}}$$

For sample 2, the average is 0.061 V.

$$\text{So } 0.061 = 10^{-8} \cdot 1.3 \cdot 1100 \text{ S}$$

$$S = \frac{0.061 \cdot 10^8}{1.3 \cdot 1100} = \underline{4270 \text{ cm./sec.}}$$

The two samples were therefore giving identical results within the limits of experimental error, and as their thickness ratio was 3:1, the diffusion length of the injected carriers was not a controlling factor.

The results for the benzaldehyde treatment are somewhat variable, but taking the maximum change in PEM voltage for each benzaldehyde treatment, as compared with the original etched surface, and averaging, sample 1 gives +0.008 V. and sample 2 gives +0.011 v. Only two instances of a fall in voltage, of -0.002 and -0.005, were observed. The indication is that the benzaldehyde treatment may produce an increase of about 0.010 v. in such experiments. Taking a mean value for the electrode spacing of 1.4 cm., and substituting in the equation

$$dV = 10^{-8} \cdot 1 \text{ B.} dS$$

$$0.010 = 10^{-8} \cdot 1.4 \cdot 1100 \text{ ds}$$

$$\text{So } dS = \frac{0.010 \cdot 10^8}{1.4 \cdot 1100} = \underline{650 \text{ cm./sec.}}$$

4.7 Measurement of the effect of benzaldehyde on photoelectric current output from surface barrier diodes

4.7.1. Apparatus. Slices of 4 ohm-cm., n-type germanium, copper plated on one side were used for the experiments. The slice was clamped in a base clip and the surface of the germanium was contacted by a pivoted assembly carrying a Pt-Ru whisker under a pressure of about 2g. The assembly was similar to that used for the rectification tests described in Final Report 1962 and illustrated in Fig.7 of that report. A 50 μ A meter was connected between the whisker and the copper base contact on the germanium. This meter had an internal resistance of about 1200 ohms. A meter reading 1.5 mA and 5 mA full-scale with a very low internal resistance and a series of load resistors were also available, for reading higher currents. Illumination was provided by a 250 watt tungsten lamp with an internal, roughly parabolic reflector. The lamp was at a distance of about 15 cm. from the germanium and shining onto the surface at an angle of 45°. No attempt was made to filter out the heat radiation from the lamp, which therefore gave out a considerable amount of infra-red.

4.7.2. Procedure. The surface of the slice was first prepared by etching in CPI to give a reasonable polish. Further etching in NaOCl/NaOH mixture was usually found to give a higher photoelectric output: the etch was prepared by adding a few pellets of sodium hydroxide to 20 ml. of 10% sodium hypochlorite solution. The surface of the slice was treated for about 5 minutes in the etch at about 40°C., giving a fairly rough surface with a clearly visible film of oxide.

After clamping the sample, the whisker was lowered into position and the base-plate tapped several times to stabilize the position of the contact. The lamp was then switched on for a short period to observe the photocurrent. Only short periods of illumination were employed, to avoid overheating the sample. However, immediately after surface preparation it was useful to allow the sample to become warm, as the maximum output was only obtained after about 1 minute of illumination; this was attributed to a drying out from the surface film of traces of water and solvent. The etched surfaces normally gave a constant output on illumination, but when benzaldehyde was added, the output varied with time, so that it was necessary to record the photocurrents at several time intervals.

In experiments where polycyclic hydrocarbons were tested as stabilizing agents, these were added as a solution in a few drops of benzene, before the addition of benzaldehyde to the surface. One drop of benzaldehyde was used in each experiment and allowed to spread out over the slice to form a thin film surrounding the whisker contact.

A comparison test was made, using a p-n junction prepared by alloying. A small piece of gallium was placed on the etched surface of a slice of 4 ohm-cm. n-type germanium, which was heated to about 300°C for 5 minutes in a protective atmosphere, then allowed to cool slowly. The excess gallium was dissolved away in dilute hydrochloric acid, leaving a small depression in the surface containing a p-n junction formed by the re-growth of germanium from gallium solution. The junction was finally cleaned by a very brief etching in CPI etch. Photoelectric tests were carried out on this junction diode, contacting the p-layer with the Pt-Ru whisker. It was considered that the thin p-layer, formed by re-growth from the gallium, would give a good photodiode.

The results obtained in these measurements are recorded below.

4.7.3. Photocurrent measurements on n-type germanium
4 ohm-cm. Ge, surface barrier diode, Pt-Ru whisker

<u>Expt.</u> <u>No.</u>	<u>Surface treatment</u>	<u>Time</u> <u>Mins.</u>	<u>Photo</u> <u>current</u> <u>μA.</u>	<u>% increase</u> <u>in current</u> <u>due to ben-</u> <u>zaldehyde</u>	<u>Remarks</u>
1	CP1 etch		12.5		
2	CP1 etch + Ph.CHO	1 2 5	5 5 7.5 5	0 50 0	
3	Wash with acetone + Ph.CHO + anthracene	2 5 10	2.5 5 7.5 0	100 200	
4	Wash with acetone + Ph.CHO	1 5	0 2.5 2.5		
5	NaOCl/NaOH etch + Ph.CHO	1 5 7 10 13 15 20	5 12.5 20 9 10 10 7.5 7	150 300 80 100 100 50 40	After 1 min. illumination
6	Wash with acetone + Ph.CHO + anthracene	1 2 3 5 10 15 90	7 10 12 12.5 12.5 15 17 17	43 71 79 79 114 142 142	After 1 min. illumination
7	Wash with acetone + Ph.CHO	1 2 5 7 10 13 20	17 30 35 30 17 12.5 12 12	76 106 76 0 -27 -29 -29	

<u>Expt.</u> <u>No.</u>	<u>Surface treatment</u>	<u>Time</u> <u>Mins.</u>	<u>Photo</u> <u>current</u> <u>μA.</u>	<u>% increase</u> <u>in current</u> <u>due to ben-</u> <u>zaldehyde</u>	<u>Remarks</u>
8	Wash with acetone + Ph.CHO + fluorene		17		
		1	30	76	
		3	25	47	
		5	17	0	
		7	17	0	
		10	17.5	3	
		15	17.5	3	
		17	18	6	
		20	18	6	
9	Wash with acetone + Ph.CHO + Phenanthrene		17.5		
		1	30	71	
		3	30	71	
		5	25	43	
		8	17.5	0	
		10	17.5	0	
		15	7	-60	
		20	3	-83	
10	Wash with acetone + Ph.CHO + acenaphthene		8		After 2 min. illumination
		1	22	175	
		3	13	62	
		5	15	87	
		15	15	87	
		20	10	25	
11	Wash with acetone + Ph.CHO + coronene		10		Output appear- ed suddenly after 30 sec. illumination
		1	20	100	
		2	22.5	125	
		5	17.5	75	
		7	7.5	-25	
		10	8	-20	
		12	8	-20	
		20	7	-30	
12	Wash with acetone + Ph.CHO + anthracene				Output appear- ed after 30 sec.
		1	12.5	67	
		2	12.5	67	
		5	13	73	
		7	10	33	
		10	5	-33	
		15	3	-60	
13	Na.OCl/NaOH etch + Ph. CHO		20		Output appear- ed after 20 sec.
		1	30	50	
		3	20	0	
		5	12	-40	

<u>Expt.</u> <u>No.</u>	<u>Surface treatment</u>	<u>Time</u> <u>Mins.</u>	<u>Photo</u> <u>current</u> <u>μA.</u>	<u>% increase</u> <u>in current</u> <u>due to ben-</u> <u>zaldehyde</u>	<u>Remarks</u>
14	Wash with acetone + Ph.CHO + anthracene	1	5		
		5	12	140	
		10	10	100	
		15	8	60	
			5	0	
15	Wash with acetone + Ph.CHO + carbazole	1	10		
		3	20	100	
		5	18	80	
		5	17.5	75	
		10	7	-30	
		15	7	-30	
		20	3	-70	
16	Wash with acetone + Ph.CHO + phenanthrene	1	7		
		5	17	143	
		10	17	143	
		10	12	71	
		15	3	-57	
		20	3	-57	
17	Wash with acetone + Ph.CHO	1	5		
		2	18	260	
		5	17.5	250	
		5	12.5	150	
		10	3	-40	
		15	3	-40	
		20	5	0	
18	NaOCl + NaOH etch + diphenyl picryl hydrazyl + Ph. CHO	1	17		
		2	17		
		1	27.5	62	
		2	25	47	
		8	15	-12	
		15	12.5	-26	
		20	7	-59	

<u>Expt.</u> <u>No.</u>	<u>Surface treatment</u>	<u>Time</u> <u>Mins</u>	<u>Photo</u> <u>Current μA.</u>	<u>Power RI²</u> <u>μW.</u>	<u>Remarks</u>
19	Wash with acetone		40	0.016	Load 10 ohms
			40	0.064	" 40 "
			35	0.122	" 100 "
			32	0.204	" 200 "
			30	0.45	" 500 "
			27	0.725	" 1000 "
20	+ Ph.CHO		75	0.056	Load 10 ohms
			70	0.196	" 40 "
			60	0.360	" 100 "
			55	0.606	" 200 "
			50	1.25	" 500 "
			35	1.22	" 1000 "

4 ohm-cm Ge, gallium doped junction, 0.5 mm. diameter

<u>Expt.</u> <u>No.</u>	<u>Surface treatment</u>	<u>Time</u> <u>Mins</u>	<u>Photo</u> <u>Current</u> μ A.	<u>% increase in</u> <u>due to</u> <u>benzaldehyde</u> <u>circuit</u>	<u>Remarks</u>
21	Alloyed junction + Ph.CHO		1170		Load 40 ohms
		1	1340	14.6	
		2	1500	28	
		3	1670	43	
		4	1670	43	
		5	1670	43	
		7	1340	14.6	
		10	1000	-14.6	
		13	1240	6	
		15	1240	6	
		18	1500	28	
		20	1500	28	
22	Wash with acetone		750		Load 40 ohms
		3	1000	33.3	
23	Wash with acetone	1	2700		Load 10 ohms
		3	2760		
				<u>Power RI²</u> <u>μW.</u>	
			2000	40	Load 10 ohms
			1200	57.5	" 40 "
			700	49	" 100 "
			350	24.5	" 200 "
			150	11.25	" 500 "
			80	6.4	" 100 "

It should be noted that the activity of the surface varied from experiment to experiment and from point to point on a given surface, in experiments 1 to 18. The absolute values of the photocurrent therefore shows some variability, but the percentage increase for the addition of benzaldehyde should be a more significant parameter. Experiment No. 19, using the gallium junction showed some random fluctuation in current during the run, probably due to the contact resistance of the Pt. whisker on the p. layer.

The general picture given by these results is that the enhanced photocurrent produced by the benzaldehyde declines rapidly after 7 to 10 minutes (with occasional exceptions, e.g. Expt. 5). The addition of some polycyclic hydrocarbons may extend the period of enhanced photocurrent, although the effect is very variable.

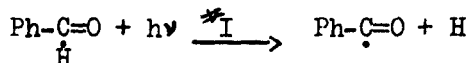
5.0 DISCUSSION OF CHEMICAL RESULTS

5.1. Evidence for a number of reaction products of the benzaldehyde oxidation

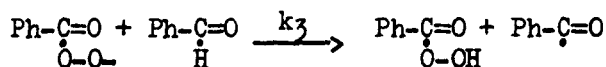
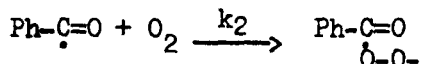
5.1.1. The investigations carried out by various workers on the benzaldehyde oxidation have been reviewed in Final Report 1962, Sect. 5.1. All the published papers agree on the initial formation of perbenzoic acid and the rapid decomposition of this product with the formation of benzoic acid (3)(33)(34)(35)(36) Wittig and Pieper (35), Waters and Wickham-Jones (34) and Mulcahy and Watt (36) have been mainly concerned with determining the mechanism of the decomposition of the perbenzoic acid and other end-products of the reaction are not considered. This approach is probably justified, as the experiments were carried out under conditions where the effect of surfaces on the course of the reaction was small.

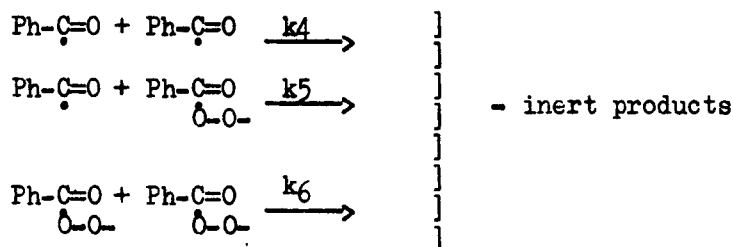
5.1.2. Ingles and Melville (37) studied both the chain propagation and termination of the reaction in n-decane solution. The solid reaction products were found to be partly peroxidic. In the plotting of \log_{10} (relative rate of oxidation) against \log_{10} (intensity of radiation), a straight line graph was obtained, with a gradient of 0.5. The gradient showed that the intensity exponent in the kinetic equation was 0.5, and therefore the termination reaction was bimolecular. The progress of the photochemical reaction was described as follows:-

Photochemical initiation,



Chain propagation,



Termination

It was concluded that if the reaction chains were long, then at the high oxygen pressures used, the rate determining step was the reaction of the peroxy radicals with the aldehyde molecules, and the main terminating reaction was the interaction of two peroxy radicals. The photo-rate was given by

$$\left(\frac{dC}{dt}\right)_p = k_3 \cdot k_6^{-\frac{1}{2}} [\text{Ph.CHO}] \cdot (I)^{\frac{1}{2}}$$

where $\left(\frac{dC}{dt}\right)_p$ is the photo-rate

k_3 is the velocity coefficient for the interaction of peroxy radicals and aldehyde molecules.

k_6 is the velocity coefficient for the termination reaction between two peroxy radicals.

I is the radiation intensity.

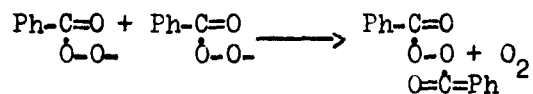
The values found for the velocity coefficients were

$$k_3 = 1.91 \times 10^3 \text{ mol. l}^{-1} \cdot \text{sec}^{-1}.$$

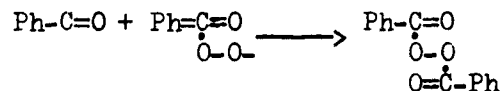
$$k_6 = 2.1 \times 10^8 \text{ mol. l}^{-1} \cdot \text{sec}^{-1}.$$

Ingles and Melville decided that the termination velocity constant k_6 was related to steric factors.

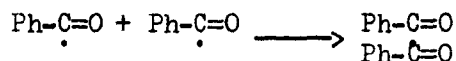
5.1.3. We would therefore expect to find in the reaction products some of the product of the terminating reaction between two peroxy radicals. The most obvious product would be dibenzoyl peroxide:-



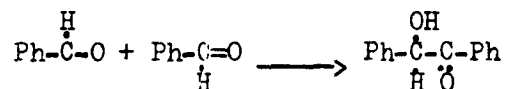
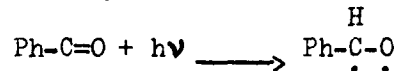
This product might also be formed in the reaction between benzoyl and peroxy radicals but on a smaller scale:-



The same reaction might also give benzil and oxygen. The terminating reaction between two benzoyl radicals would probably result in the formation of benzil:-



The photolysis of benzaldehyde in the absence of oxygen is reported (3) to yield benzoin as the main product:-



There was therefore some possibility of this compound also being present.

5.1.4. In the reactions we have studied, the surface was a predominant factor in controlling the rate of reaction by terminating the reaction chains. One would therefore expect to find reasonable quantities of the products of the characteristic terminating reactions. The deficiency in the amount of benzoic acid produced, compared with the amount of benzaldehyde consumed, as shown in Final Report 1962, Sect. 5.2.11, confirms that other products are present.

5.2. Interpretation of results obtained

5.2.1. Detection of benzoic acid and perbenzoic acid on the gas chromatograph.

Our experiments have shown that benzoic acid, with a boiling point of 249°C . has a sufficiently high vapour pressure at 110°C . to pass through the column in a reasonably short time. The ionization detector is obviously very insensitive to benzoic acid and was not capable of detecting the amounts normally obtained in our experiments. Similarly, perbenzoic acid, present in even smaller amounts, could not be detected, for the same reason. The failure to detect these compounds was clearly a deficiency which could be remedied by further experiments with other types of sensitive detector. We are now experimenting with the flame ionization detector, but unfortunately this detector was not available when the measurements were being made.

5.2.2. Variation in concentration of perbenzoic acid

The change in concentration of perbenzoic acid during a typical run is shown in Fig. 5, the graph being based on the electrometric titration curves of Fig. 4. While the general pattern of the rapid rise and gradual fall of the perbenzoic acid concentration is similar to that described by Waters and Wickham-Jones (34) and Mulcahy and Watt (36), the change took place in a much shorter period in our experiments. Fig. 5 shows that the concentration was very small after 25 minutes, although the other workers report considerable concentrations still present in their systems after this time. The rapid decline of the concentration of the per-acid is clearly the result of the removal of the peroxy radicals at the germanium surface.

5.2.3. Detection of other oxidation products

The failure to detect any other stable compounds present in the oxidation products, e.g. benzil, benzoin or benzoic anhydride may once again show the limitations of the gas chromatographic equipment which was in use. A column temperature of 270°C - 300°C would have been preferable for this examination, but was not obtainable at the time of the experiments. The addition of standard amounts of benzil and

benzoin did not produce any peaks at the column temperature of 212°C. There appears to be no published information on the retention times of benzoic acid, benzil, or benzoin, or on the sensitivity of the ionization detector to these compounds.

However, subsequent chemical tests, reported in Sect. 3.7, suggest that little or no benzil or benzoin can be present, and the product of the terminating reaction is probably dibenzoyl peroxide only. The oxidation reactions confirm the presence of a peroxide, but not its exact identity.

6.0 Discussion of Physical Results

6.1. The discussion of the contact potential, or as we will now call them, surface potential, measurements will be left until last, as the subject is of a more complex and controversial nature than the surface recombination and photoelectric work: furthermore, it is not directly concerned with the original objects of this research program, although it is of considerable fundamental importance.

6.2. Surface recombination rate

6.2.1. It is clear from the photoelectromagnetic effect measurements, that once a surface with a reasonably low recombination rate has been prepared, it is not easy, using a simple procedure, to make accurate estimates of small changes. This is because the PEM. voltage tends towards a constant maximum or a constant minimum reading for low values of S , depending on whether the opposite surface is ground or etched. The more complex procedure of van Roosbroeck (27)(32) would be necessary to obtain more accurate measurements, but as we were mainly interested in comparative results the more complex measurements were not justified.

6.2.3. Our estimates of the surface recombination velocity on each of the ground surfaces, 4200 cm./sec. and 4270 cm./sec. are reasonable approximations for the simplified method, and rather better than the value of 2000 cm./sec. quoted in the paper by Buck and Brattain (14): the generally accepted value for ground surface has been about 10,000 cm./sec. However, later and more accurate measurements (15)(27)(32) suggest

that values in the region of 50,000 cm./sec. are more correct.

6.2.4. The original etching of the surfaces of the samples by CPI was not carried out sufficiently well to give an ideal polished surface with a minimum value of S . This was done deliberately to help reveal any effects of the benzaldehyde treatment. In some of the experiments, the surfaces were deliberately contaminated with copper, but, surprisingly little effect was observed. There was generally a small, but definite, rise in PEM. voltage after benzaldehyde treatment, although the average value given is probably not very accurate, because of the small size of the voltage and its variation from one experiment to another. The maximum effect of etching, either with or without benzaldehyde treatment, was never attained until 5 minutes or more after the final washing and drying, and after a number of measurements had been taken. Samples were always washed with distilled water and acetone after treatment, and the slow improvement in the PEM. voltage was attributed to a drying-out of the oxide film on the surface. There was some evidence that samples left for 15 hours or more developed higher values of S , probably due to contamination of the surface. Assuming that the original etched surface probably had a surface recombination velocity of several hundred, the experiments suggest that a reduction to 50 or 100 cm./sec. may have been achieved. The minimum reported values for S are about 100 cm./sec.⁽¹⁵⁾ for surfaces which have been well etched until all abrasion damage has been removed.

6.2.5. While it is not possible to place a very definite figure on the decrease of the surface recombination velocity after treatment, such a decrease is supported by our conclusions on surface barrier rectification, given in Final Report 1962, Sect.6.2. The rectification tests showed a pronounced increase in the reverse impedance of surface barrier rectifying contacts after benzaldehyde treatment. From present theories of rectification, due to Bardeen⁽³⁸⁾, it was concluded that as the height of the potential barrier was largely determined by the space charge set up by the concentration of surface states, so the benzaldehyde treatments must be able to create a permanent increase in the height of the barrier. Other workers⁽¹³⁾⁽³²⁾⁽⁶⁷⁾⁽⁶⁸⁾⁽⁶⁹⁾⁽⁷⁰⁾⁽⁷¹⁾⁽⁷²⁾ have shown that the surface recombination velocity on both

n- and p-type germanium is at a minimum when the surface barrier is at a maximum. Both rectification and surface-recombination tests therefore indicate some beneficial effect from benzaldehyde treatment.

6.2.6. The change in the height of the surface barrier is probably produced by an increase in the thickness, or modification of the structure of the oxide film, in such a way that more acceptor surface states are created. Our measurements of contact potential have shown (Sect.4.5) that the formation of a thick oxide film, by anodising for example, will help to produce a higher potential from adsorbed water molecules: this potential depends on the number of molecules adsorbed, and therefore, on the concentration of surface states in or on the oxide.

6.2.7. The tests for any cleaning action of benzaldehyde on the germanium were inconclusive, as it was difficult to measure any significant changes in the PEM. voltage after adding contamination, in the form of copper salts. However, if we consider indirect evidence from Final Report 1962, Sect. 5.2.12, we find that irradiated benzaldehyde produces a very rapid attack on mercury to give a compound which appears to be dimercury dibenzoate $C_6H_5.CO.O.Hg.Hg.O.CO.C_6H_5$. This attack is probably the direct action of perbenzoate radicals on the metal. It would therefore be expected that metallic contamination on a germanium surface might also be attacked, provided it was not too strongly combined with the oxide film, and effect some cleaning action. It is well known that semiconductor surfaces are very easily contaminated by metallic impurities from etching solutions and washing liquids. (73)(74). For example a fraction of a monolayer of gold on a silicon surface may seriously reduce the minority carrier lifetime (75). Various methods of removing metallic surface contamination have been studied in the past, including treatment with potassium cyanide solution or ethylenediamine-tetra-acetic acid and its salts. The benzaldehyde method might well be an improvement on these techniques and easier to use: it would have the additional advantage of producing desirable electrical characteristics at the surface, at the same time. The main precaution necessary

would be to use a highly purified solvent for the final washing of the surface. A final treatment of transistor or diode structures before encapsulation, using irradiated benzaldehyde, would require no elaborate precautions against the corrosion of metal parts.

6.3. Photoelectric effects

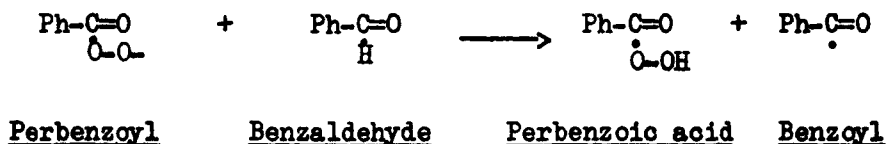
6.3.1. The increase in photoelectric current generated by a surface-barrier diode on the addition of benzaldehyde to the surface is clearly a very well-defined phenomenon. A maximum increase of between 70 and 300% was observed in the series of experiments carried out. The increase in current was not permanent, and usually disappeared after about 7 to 10 minutes after the application of the benzaldehyde; subsequently, the current fell to a lower value than normal. There were some exceptions to this rule, when polycyclic hydrocarbons were added, but these are discussed later.

6.3.2. The initial enhancement of the photocurrent for a short period suggests that the initial photochemical reaction of the benzaldehyde was responsible. The data presented in Final Report 1962 Sects. 3.0 and 5.0 and Sect. 3.8 of the present report show that the concentration of perbenzoic acid was at a maximum within a few minutes of the start of irradiation and declined rapidly within 10 minutes. The rapid change in the U.V. transmission of a 0.0125 cm. benzaldehyde film during the first 7 minutes of irradiation has been described in Sects. 3.7.3 and 5.2.13 of Final Report 1962. It was shown that the film transmission rose from an initial value of 38% to 80% in 7 minutes, after which it remained reasonably constant (allowing for some light scattering by solid products in the later stages of the reaction). The period of strong absorption of radiation and maximum concentration of peracid correspond closely to the period during which the photocurrent increases to a maximum.

6.3.3. In some of the experiments we observed a delay of between 20 and 60 seconds before any appreciable photocurrent would be obtained. For the untreated surfaces this could be attributed to a drying out of the oxide film following etching and washing: with benzaldehyde added, it may have

been the manifestation of an incubation period in the photochemical reaction, as studied by Mulcahy and Watt (36). The enhanced photoelectric efficiency could be interpreted in terms of the theories of charge-transfer adsorption, as put forward by a number of workers (39)(40)(41) and particularly by Krusemeyer and Thomas (42). The subject of charge-transfer catalysis has been discussed in Sect. 6.2.16 of Final Report 1962. The idea of charge transfer catalysis was first advanced by Wagner and Hauffe (43) and later elaborated by Garner et al. (44), Volkenshtein (45), Hauffe (46) and by Hauffe and Schlosser (47). An excellent analysis of the subject has been given more recently by Garrett (48). Briefly, if there is a reaction between two adsorbed species at the semiconductor surface, one species, A, capable of ionizing to become an acceptor and one species, D capable of ionizing to become a donor, then the reaction $A + D \longrightarrow AD$ may proceed with a net exchange of electrons from the semiconductor to A and to the semiconductor from D. More complex reactions are also possible, e.g. $A + B \longrightarrow C + D$, where A and D are again acceptor and donor species, but on opposite sides of the equation.

6.3.4. In the early stages of the benzaldehyde photo-oxidation, the most likely reaction, after the initial formation of perbenzoyl radicals (see Sect. 5.1.2) is the following:-



In this system it is likely that the perbenzoyl radical will act as an acceptor and the perbenzoic acid or the benzaldehyde as a donor. The reaction will proceed with the injection of hole-electron pairs into the inversion layer at the surface of the n-type germanium. The holes and electrons are separated by the space-charge and produce a flow of current in an external circuit, the whisker contact to the surface becoming positive and the germanium negative.

6.3.5. The highest output of photocurrent, in the absence of benzaldehyde, was given by a surface etched in NaOCl/NaOH mixture, to give a visible oxide film at the surface. Referring again to the results of our experiments on contact potential, Sect. 4.5, it is probable that such oxidised surfaces have a high concentration of surface states at the oxide surface. The higher photocurrent output suggests that some of the current carriers, at least, may be generated from the surface states, whose energy levels lie in the forbidden gap between the valence and conduction bands: the generation of carriers from these states by photons would require less energy than the normal transitions between valence and conduction bands. The presence of trapping centres (which again, could be the same surface states), which produce enhanced photoconductivity (49)(50)(51)(52), would be of no advantage in a photovoltaic cell.

6.3.6. The generation of current in a photovoltaic cell is illustrated in Fig. 15. Fig. 15a shows the equilibrium positions of the energy bands across a typical p-n junction, with the Fermi level continuous across the barrier. When the open-circuit junction is illuminated, hole-electron pairs are generated, and diffuse about in the crystal; the effect of the space charge is to cause holes to travel towards the p-type layer and electrons towards the n-type layer, so constituting an internal current. The junction is thus biased in the forward direction, and generates an internal opposing current until equilibrium is attained; this situation is shown in Fig. 15b. The maximum voltage generated, V , is equal to the difference of the Fermi levels on the two sides of the junction during illumination. If a finite load R_L is connected across the junction, some of the current will flow through it, and the junction will have a forward bias which is obviously less than V , the maximum attainable. The equivalent circuit of an irradiated junction is shown in Fig. 16 (53)(54)(55), in which the radiation source is represented by the constant current generator i_g and the junction is represented by the non-linear impedance R_j , an internal series resistance R_s and an internal shunt resistance R_{sh} . The relation between the load current i_L and the

output voltage V_L across the load has been shown to be given by the equations:-

$$V_L = V - i_L R_s$$

$$i_L = \frac{V}{R_s + R_L} = i_s - i_0 (\Lambda^V - 1) - \frac{V}{R_{sh}}$$

where i_s is the short-circuit current

i_0 is the minority carrier current (mainly from thermal generation)

and $\Lambda = e/kT$.

The relation between i_s and the number of incident photons which have energies sufficient to generate hole-electron pairs, $N(E_g)$, is given by

$$i_s = (1-K)(1-T) eQN(E_g).$$

where K is the reflection coefficient,

T is the fraction transmitted,

Q is the fraction of the minority carriers generated which successfully diffuse across the barrier and give rise to the effect.

Q is a function of minority carrier diffusion length L , the semiconductor thickness d , the adsorption coefficient for the radiation α and the surface recombination velocity S .
(56)(57)

6.3.7. In our experiments, the main controlling factors will be $N(E_g)$ and S . We have shown in Sect. 6.2. that S tends to be smaller after benzaldehyde treatment, but is doubtful whether a significant decrease would occur in the first 5 minutes of irradiation. Referring back to Sect. 6.3.4., we have suggested that the photochemical reaction will inject hole-electron pairs into the surface layer of the semiconductor.

As a chain reaction is involved with a quantum yield of about 8 (See Final Report 1962, Sect. 3.7), we would expect each reacting quantum to give 8 hole-electron pairs. This introduces another term η for the quantum efficiency of the generating process in the above equation for i_s , which then becomes:

$$i_s = (1-K)(1-T) eQ\eta N (E_g).$$

When comparing the photo-diodes, with and without benzaldehyde, the only factor which will be appreciably different is η . Referring to the experimental results given in Sect. 4.7.3, we find that the maximum increase in photocurrent which was observed was 300%, i.e.

$$i_1 (\text{benzaldehyde}) = 4 i_1 (\text{untreated}).$$

Allowing for the minority carrier current and internal shunt current terms, the ratio of i_1 (benzaldehyde) to i_1 (untreated) will then be rather less than 4:1, i.e. η is rather less than 4. We have shown in Final Report 1962, Sect. 3.7.3, that the transmission of a benzaldehyde film, as used in these experiments, averages about 60% during the first 5 minutes of irradiation: correcting for this, we find that η is now somewhat less than 6. This agrees fairly well with the chemical figures of 7 to 9 for the quantum efficiency for a thin film, as given in Final Report 1962, Sect. 3.7. There is therefore strong evidence that the enhanced photocurrent generation is controlled by the quantum efficiency of the benzaldehyde autoxidation.

6.3.8. It is interesting to make an estimate of the conversion efficiency of the surface barrier diodes which were used for these experiments. Experiment 19 shows that the untreated unit gave a maximum power output of 0.725 μ W into a 100 ohm load. The power input to the lamp was 250 watts, and assuming a typical efficiency of 15%, the radiated light energy was 37.5 watts. The equation for i_s contains a term Q , which is a function, amongst other parameters, of minority carrier diffusion length L and semiconductor thickness d . In the case of a surface barrier diode, it is probably incorrect to visualize a hemisphere, of radius L , surrounding the point contact and containing the flux of holes and electrons, created by the

illumination. Because of the surface structure, it is more realistic to imagine that the carriers tend to follow a very thin surface channel. If this is so, we can say that all the flux of holes and electrons is passing through the wall of a cylinder, radius L and depth, say 10^{-4} cm., the dimension of the space-charge region. The effective collecting area of a point contact (with no applied field) is approximately the spreading-resistance zone, with a radius equal to the diameter of the point.⁽⁵⁸⁾ Taking a typical value for the diameter of the point contact of a Pt whisker, e.g. 5×10^{-4} cm, the collecting area is the wall of a cylinder, radius 5×10^{-4} cm and 10^{-4} cm. deep.

The fraction of the flux of holes and electrons collected by the point contact was therefore

$$\frac{2 \pi 5 \times 10^{-4} \cdot 10^{-4}}{2 \pi 6.65 \times 10^{-2} \cdot 10^{-4}}$$

where 6.64×10^{-2} is the diffusion length L .

L was calculated from the relation $L = (D\tau)^{\frac{1}{2}}$

where D is the diffusion constant = $44 \text{ cm}^2 \text{ sec}^{-1}$
for holes

τ is the minority carrier lifetime = 100
microsecs. for the sample of Ge used.

The aperture of the lamp was 12 cm., and the roughly parabolic reflector gave a reasonably parallel beam so that the effective radiating area was $\pi \times 6^2 / \sin 45^\circ$ for a 45° mounting. The light flux falling on a circle of radius L was therefore

$$37.5 \times \frac{\pi (6.64 \times 10^{-2})^2}{\pi \cdot 6^2 / 0.707} \text{ watts, and the}$$

flux intercepted by the point contact was

$$\begin{aligned} & 37.5 \times \frac{\pi (6.64 \times 10^{-2})^2}{\pi \cdot 6^2 / 0.707} \times \frac{2 \pi \cdot 5 \times 10^{-4} \cdot 10^{-4}}{2 \pi \cdot 6.64 \times 10^{-2} \cdot 10^{-4}} \text{ watts,} \\ & = \underline{2.5 \times 10^{-5} \text{ watts.}} \end{aligned}$$

As the maximum power output was 7.25×10^{-7} watts the efficiency was approximately 3.5%. With the increased power output, recorded in Expt. 20, of $1.25 \mu\text{W}$, on addition of benzaldehyde, the efficiency increased to approximately 5%. These estimates may be low because of the number of assumptions made in the calculations, especially if the flux of injected holes and electrons spreads further into the bulk of the material than we have assumed.

6.3.9. A comparative calculation can be made for the alloy diode structure, whose output is recorded in Expt. 21. Experiments 21 and 22 suggest that the addition of benzaldehyde to the alloy diode increased the output by 30 to 40%, which is considerably less than the range 70 to 300% recorded with the surface-barrier diodes. This is explained by the fact that the benzaldehyde would have given enhanced injection only around the edge of the junction. Less assumptions have to be made about the active area of the alloy junction, which is approximately equal to its geometrical area.

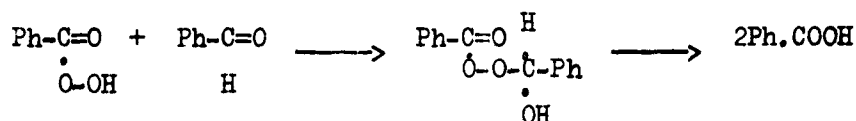
The junction in this case was 0.05 cm. in diameter giving an area of $1.97 \times 10^{-3} \text{ cm}^2$, and the light flux intercepted by the junction was

$$\begin{aligned} & 37.5 \times \frac{\pi (2.5 \times 10^{-2})^2}{\pi 6^2 / 0.707} \text{ watts} \\ & = \underline{4.6 \times 10^{-4} \text{ watts}} \end{aligned}$$

The maximum output obtained was $57.5 \mu\text{W}$, so the efficiency was approximately 12.5%.

The maximum output current into a 10 ohm load, as recorded in Expt. 23, was nearly 3mA.: this represents an output capability of about 1.5 amps.cm^{-2} , for this type of junction.

6.3.10 The stabilization of output, sometimes achieved by the addition of polycyclic hydrocarbons, particularly anthracene, is not readily explained. It is possible that, as the maximum photocurrent output is associated with the presence of perbenzoic acid, the hydrocarbon may interfere with the acid-catalyzed decomposition of perbenzoic acid with benzaldehyde.



This is the normal terminating reaction of the chain.

As the normal oxidation reaction proceeds, the photoelectric output, having passed its peak, falls to a lower value than was obtainable before the benzaldehyde was applied. This suggests that the products of the reaction, e.g. benzoic acid and/or dibenzoyl peroxide may reduce the number of available surface states, or produce states with unfavourable energy levels for photo-activation.

6.4 Surface potential measurements

6.4.1. Appraisal of the experiments reported in 1962

It is evident from the considerable amount of detailed work carried out in the present programme, that an over-simplified picture was presented of the early experiments. The experiments are clearly not equivalent to the classical contact potential measurements by the Kelvin method. A vibrating electrode must be used for the Kelvin measurement, otherwise the sensitivity of the method is extremely low. As we will show later, if two different phases, e.g. germanium and platinum, are put in contact through an external circuit, so that the Fermi levels are in equilibrium, the regions just outside the surfaces of these phases assume a potential difference equal to the difference in Volta potential, or contact potential. Kelvin's original method (59) was based on the principle that on breaking contact between the plates and altering the spacing, a current, detectable by an electrometer, flows to or from the plates. By connecting the plates through a potentiometer, it was possible to find an applied potential at which no current flowed when the plate spacing was altered;

the applied potential was then equal to the difference in Volta potentials or work functions of the metals. A sensitive modification of the method was first described by Zisman (60) in which one of the metal plates was made to vibrate rapidly in a direction perpendicular to its surface. The oscillating current produced was amplified and applied to an output indicator: when an opposing potential was applied to the plates from a potentiometer, a null point was found when the voltage was equal to the contact potential. This basic technique is the basis of all present versions of the Kelvin method.

Measurements have been made using a stationary reference electrode, but the initial difficulty is the exceedingly high resistance of the air or gas in the gap. This difficulty can be overcome by ionizing the gas, a method first used by Righi (61). The stationary electrode technique has been used for measuring the surface potential of films on liquids by a number of workers (62)(63)(64)(65)(66), in all cases making use of the ionized air gap. Even when water vapour is present in the gas, the resistance of the gap is apparently still extremely high, on the evidence of the erratic results recorded in Sect. 4.4.4. No provision was made for ionizing the oxygen in the original work described in Final Report 1962, but high potentials were recorded in many of the experiments. If the water is adsorbed as a charged dipole, the field external to the dipole layer is extremely small and we would not expect an appreciable charge to be induced on the platinum. However, if a potential of, say, 100 volts appeared, due to a charge between the platinum and germanium, the value recorded by the measuring equipment which we originally used would be considerably less, for the following reason: the value of the vibrating capacitor used in the input circuit was about 30 pf., while the capacitance of the platinum-germanium system was only about 2 pf., and the charge would have to be divided between the two capacitors in the ratio of the capacitances. Thus, the charge on the 2 pf. capacitor would occupy a final capacitor of 32 pf., and by the usual electrostatic relation $Q=CV$, the voltage V would decrease to 1/16 of its original value, or about 6 volts. If however, the platinum was connected through to a source of charge by an ionized gap, or other conducting path, it would be

possible to supply enough charge to produce a high potential on the whole system.

These arguments suggest that when high potentials were recorded for long periods, the platinum electrode must have had a conducting path to the charging source. In the absence of ionization, it is most likely that there existed microscopic fibres across the gap between the platinum and germanium. In the latter part of our investigation we have worked on this assumption, which was first suggested to us in discussion with Prof. F.C. Frank. This arrangement provides a logical explanation of how steady potentials could be recorded in the Pt/Ge system, but does not directly explain the high values of up to 100 volts which were recorded. There is no doubt that these potentials appeared when moisture was introduced into the oxygen and disappeared when it was removed, and no appreciable potential could be obtained with a block of brass: the measurements did not therefore relate to the properties of the fibres in the gap. A discussion of the validity of the actual voltages recorded is given in the following section.

6.4.2. Evaluation of the accuracy of voltage measurements by the null method.

The null method of voltage measurement originally used has been described in Final Report 1962, Sect. 4.9.1. and is shown in Fig. 9. Two variations of the classical backing-off circuit are shown in Figs. 10a and 10b. The parallel circuit of Fig. 9 was the only one which would give satisfactory results in the original measurements, while the more conventional series circuits shown in Fig. 10 did not appear to work, i.e. little response could be obtained when the potentiometer was adjusted. It is interesting to evaluate the behaviour of these circuits when there is a conducting path of, say, 10^{10} ohms between the platinum and germanium. In Fig. 9 we see that the backing-off circuit will place an opposing field across the input to the vibrating capacitor, but the voltage applied to the system will be divided down by 10^{11} ohms in series with the 10^{10} ohms gap resistance. On the other hand practically all the voltage from the source, the germanium surface, will appear across the input. Thus, if there is a surface potential of 100 volts

at the germanium, about 90 volts will appear across the input to the amplifier, but the application of 100 volts from the potentiometer will apply only about 10 volts opposing bias to the input. Applying a similar argument to the operation of the classical backing-off circuit Fig. 10a we find that about 9/10 of the voltage from the potentiometer will be applied, and for Fig. 10b, the whole of the voltage will be available: the whole of the voltage from the source appears across the amplifier in each case. Therefore the classical backing-off circuit shown in Fig. 10 is desirable if there is a conducting path across the measuring terminals, although in practice, it was found to be extremely sluggish in operation. This discussion shows why it was imperative to use a direct-reading instrument for the later experiments, and why the potentiometer voltages recorded in Final Report 1962 did not represent the correct potentials at the germanium surface. It appears likely that the high potentials were in the region of 10 volts, rather than 100 volts, and this conclusion is supported by one reading, in excess of 10 volts, recorded on the Wayne-Kerr electrometer.

The calculations, previously carried out, of the density of adsorbed water molecules, based on maximum potentials of 100 volts are therefore incorrect (cf. Sect. 6.2.15, Final Report 1962). A printing error also appears in this section, where the total charge q is given by the equation $q = C.V \times A$, and not as printed. The basis of calculation, involving a simple charge on a capacitor formed by the platinum and germanium, is not valid in the light of our recent work and the discussion in this section. A more valid calculation will be given later.

6.4.3. The measurements described in Sects. 4.3 and 4.4 are representative of the results obtainable with a gap of very low conductivity, special precautions having been taken to prevent surface contamination. These results are erratic and inconclusive, except in a few cases where accidental contamination enabled potentials in the region of 500 mV to be recorded. The material bridging the gap in these cases could not be seen with a lens and strong illumination.

6.4.5. The potential readings, using a glass fibre probe to contact the germanium surface, appear to be reliable and reproducible, and representative of the true surface potential of the germanium. The variations of the potential with time in wet and dry ambients, under short-circuit conditions and with applied fields, provide valuable information on the density and relaxation times of the surface states, as will be shown.

Before we can interpret the significance of the potentials obtained, it will be useful to discuss the relationships between the band structure and potentials in a semiconductor system.

6.4.6. Potential and band structure relationships

6.4.6.1. Any phase can be regarded as having a characteristic inner electric potential ϕ , which is characterized by the distribution of space charges and polarization within the material. The outer electric potential of the same phase is the potential just outside the uniform bounding surface at a distance just beyond the range of image forces (i.e. just over 10^{-4} cm.), and is designated by ψ . At the bounding surface of a phase we may expect layers of charges or dipoles to occur, and as a result, a change in the average electrostatic potential will occur from a point in the bulk of the phase to a point at the outer electric potential. The potential change is the surface electric tension χ . We then have the relationship, $\phi = \psi + \chi$.

The contact potential difference, or Volta tension V between two phases 1 and 2 is defined by the outer potentials:

$$V = \psi_1 - \psi_2$$

6.4.6.2. The accepted energy level diagram for an n-type semiconductor with acceptor surface states is shown in Fig. 17. E_f is the Fermi level, or electrochemical potential, E_c and E_v and the energy levels corresponding to the edges of the conduction and valence bands, respectively, and E_i is the mid-gap or intrinsic Fermi level. An oxide layer is shown to be present, with conduction and valence bands at

arbitrary positions outside the energy gap of the bulk of the crystal.

The electrochemical potential E_f is equivalent to the work required to transfer an electron from infinity to a point in the bulk of the semiconductor, and is the sum of two terms:

(a) Work due to the interaction between the electron and the bulk of the semiconductor, which is the chemical potential E , and depends only on the chemical constitution of the semiconductor.

(b) Work due to the presence of surface dipoles, or free charges at the semiconductor surface. This is equivalent to $e\phi$ for an electron.

Therefore, $E_f = E + e\phi$

ϕ can be represented as $\psi + \chi$, where ψ represents the potential due to free charges on the surface of the semiconductor and χ the potential due to surface dipoles, giving the relation

$$E_f = E + e (\psi + \chi)$$

6.4.6.3. One important factor in calculations involves the potential difference between a point in the interior of the semiconductor and a point at the semiconductor - oxide interface. This is the surface-barrier height Y defined, in units of kT as:

$$Y = \frac{e}{kT} (\phi_b - \phi_s)$$

where ϕ_b is the inner potential in the bulk of semiconductor

ϕ_s is the inner potential at the interface.

6.4.6.4. For an electrical double layer at a semiconductor surface, we can consider two parallel sheets of charge density Q per unit area, spaced at a distance d from each other. The electric field strength normal to the charge sheet is given by Gauss' law, $x = 2 \pi Q$. In the regions outside the

parallel sheets there is no field, but in between, the fields due to the two charged layers added together to give a uniform field $4\pi Q$. The potential step across the layer is then $\phi = 4\pi Qd$. Variations of the simple double layer may occur at semiconductor surfaces. For example, if the charge sheet nearest the semiconductor surface is replaced by a uniform volume distribution of charge in a layer of finite thickness, and charge density Q per unit area, the potential drop across d is still the same, $4\pi Qd$, but there is also a potential drop within the distributed charge sheet, in accordance with Poisson's equation :

$$\nabla^2 \phi = - \frac{4\pi}{\epsilon} \rho \quad (x,y,z)$$

Where ϵ is the dielectric constant

ρ is the volume charge density

This system is operative for a semiconductor with charges in surface states, residing on the outside of an oxide layer of thickness d . The potential drop in the distributed charge sheet is the inner potential difference $(\phi_b - \phi_s)$.

6.4.6.5. The electronic work function of a neutral phase is defined as the work necessary to remove an electron from the interior of the phase and place it at rest outside the semiconductor at point where the electric potential is equal to ϕ . For a semiconductor without surface states the work function is then

$$-W_0 = E + e\chi$$

The presence of surface states will affect the work function through the term χ , by the potential shift in the space charge region, giving

$$W = W_0 - e (\phi_b - \phi_s)$$

If there are adsorbed impurities with oriented dipoles, this will also alter the work function by an increment $d\chi$. If there is an oxide layer with charges in the slow states on the outside of the layer, then there is an additional potential drop ϕ_1 in the oxide. The general expression is therefore,

$$W = W_e - e [(\phi_b - \phi_s) + d\chi + \phi_1]$$

6.4.6.6. Fig.18 shows potential diagrams for the semiconductor metal system. When the metal and semiconductor are separated, as in A, for zero field in the gap ($\psi_1 - \psi_2 = 0$) the Fermi levels E_{f1} , E_{f2} , differ by the amount $(W_2 - W_1)$, the difference in work functions.

The Volta potential, v or contact potential difference between two metallic phases is defined as the difference between the outer potentials of the phases, when in equilibrium, i.e. $v = \psi_2 - \psi_1$

$$\text{Since } E_f = E + e(\psi + \chi)$$

$$E_f - e\psi = E + e\chi = -W$$

$$\text{therefore } -v = \frac{1}{e} (W_2 - W_1).$$

The field in the gap is equal to V/d , where d is the gap spacing, and there is a charge on each electrode given by

$$Q_m = eV/4\pi d.$$

The inner potential difference between two metals in equilibrium is the Galvani potential, given by

$$\begin{aligned} -g = \phi_2 - \phi_1 &= \frac{1}{e} (E_1 - E_2) \\ &= \frac{1}{e} (W_2 - W_1) + (\chi_2 - \chi_1) \end{aligned}$$

For the semiconductor-metal system in equilibrium as shown in B, it is necessary to take into account the potential shift in the space-charge region of the semiconductor. The Galvani potential is given as above, but the Volta potential of the system is not equal to $1/e (W_2 - W_1)$ because the

work function of the semiconductor is modified by the inner potential difference $(\phi_b - \phi_s)_2$

$$\text{Thus } -V = \frac{1}{e} (W_2 - W_1) - (\phi_b - \phi_s)_2$$

and the Galvani potential can be written,

$$-g = -v + (\chi_2 - \chi_1) + (\phi_b - \phi_s)_2$$

The terms v and $(\phi_b - \phi_s)$ vary with the gap spacing d and so the Volta potential is not solely dependent on the properties of the electrodes.

6.4.6.7. In the presence of surface states, illustrated before and after equilibrium, in C and D, the interior of the semiconductor is screened from external fields, and this reduces the dependence of the Volta potential on the gap spacing. The Galvani potential g and the charge Q_m on the metal electrode are given as above, but in equilibrium the condition for electrical neutrality becomes

$$Q_m + Q_{sc} + Q_{ss} = 0$$

where Q_{so} is the charge residing in the space-charge region

Q_{ss} is the charge in the surface states

It can be shown that the variables d and Y can be expressed in the equation

$$\frac{d}{L_d} [F(Y, u_b) + A Q_{ss}(Y, u_b)] + Y = \text{constant}$$

where d is the gap spacing

L_d is the Debye length

Y is the surface barrier height

u_b is the bulk mobility

A is a constant

$Q_{ss}(Y, u_b)$ is derived from the surface state occupancy functions. For a high density of surface states, $Q_{ss}(Y, u_b)$ is a rapidly varying function of Y and is the dominating term in the equation. Therefore, the equilibrium value Y is almost independent of d and consequently v is also independent of d , as Y is defined as equal to $e/kT(\phi_b - \phi_s)$.

For a small gap and in the presence of surface states the Volta potential v is nearly equal to the work function difference, as shown in Fig. 18D.

6.4.6.8. Fig. 18E illustrates the effect on an external voltage V applied between the two phases. For a fixed gap the inner potential difference $(\phi_2 - \phi_1)$ between the phases is given by:

$$(\phi_2 - \phi_1) = V - g = H + (\phi_b - \phi_s)_2 + \text{constant}$$

where H is the outer potential difference $(\psi_2 - \psi_1)$ across the gap, (equal to the Volta potential v when $V=0$). The constant includes surface dipole and chemical potential terms independent of V . It is required to decide how the applied emf. is divided between the surface barrier height $(\phi_b - \phi_s)_2$ and H . Now, H is given by the equation,

$$\begin{aligned} H &= -4\pi d Q_m / e \\ &= (4\pi d / e) (Q_{sc} + Q_{ss}) \end{aligned}$$

It can be shown that the equation for V can take the form:

$$V = \left[\frac{d}{Ld} \cdot \frac{kT}{e} F(Y, u_b) + C Q_{ss}(Y, u_b) \right] + \frac{kTY}{e} + \text{constant}$$

In this equation Y and V are considered as dependent and independent variables. As $Q_{ss}(Y, u_b)$ is a rapidly varying function of Y , it follows that Y must be nearly independent of V . Thus, Y will remain nearly constant and equal to the equilibrium value Y_0 and the applied emf. will appear almost entirely across the gap. The space-charge Q is also nearly constant as Y is constant, and changes in Q_m are almost entirely balanced by corresponding changes in the surface state charge Q_{ss} .

6.4.7. Application of the potential relationships to the practical experiments.

6.4.7.1. In the practical case we have studied, of the adsorption of water molecules on a germanium surface, we have a surface with a high concentration of surface states at the oxide-gas interface. There is a oxide layer of appreciable thickness with a well-defined dipole layer at the surface, due to the adsorbed water. We have shown that, in the case of a high concentration of surface states, the Volta potential is equal to the difference in work function

between the metal and the semiconductor. Fig.19 shows the energy band and potential diagrams for the Ge/Pt system, with water adsorbed at the germanium oxide surface, before and after equilibrium. If the system is not in equilibrium, which is the condition under which the measurements have been made, the potential distribution will be similar to that in Fig.19A. It is assumed that there is no field in the gap, and in practice the gap has been almost eliminated, by contacting the end of the surface dipole layer with a glass fibre probe. We can see that the voltage across the system, apart from a small contribution χ_{Pt} , is equal to the voltage across the dipole layer $\alpha\chi$ minus χ_{Ge} , the space-charge potential.

6.4.7.2. To examine the factors involved more closely, let us consider that the Pt/Ge system is in thermodynamic equilibrium as in Fig 19B and derive the value of the Volta potential between the phases.

The Volta potential is given by

$$-v = \frac{1}{e}(W_{Ge} - W_{Pt})$$

The work functions of platinum and germanium are

$$-W_{Pt} = E_{Pt} + e\chi_{Pt}$$

$$-W_{Ge} = E_{Ge} + e\chi_{Ge}$$

where E is the chemical potential in each case and χ is the surface dipole term. The surface dipole term for germanium must be expanded, as shown in Sect.6.4.6.5, to include terms for the inner potential difference $(\phi_b - \phi_s)$, oriented surface dipoles of water $\alpha\chi$ and the potential drop in the oxide layer ϕ_1 .

$$\text{Thus } -W_{Ge} = E_{Ge} - e[(\phi_b - \phi_s) + \alpha\chi + \phi_1]$$

$$\text{Therefore } -V = \frac{1}{e}[(E_{Ge} - e[(\phi_b - \phi_s) + \alpha\chi + \phi_1]) - (E_{Pt} + e\chi_{Pt})]$$

$$= \frac{1}{e}(E_{Ge} - E_{Pt}) - \chi_{Pt} - (\phi_b - \phi_s) - \alpha\chi - \phi_1$$

This can also be expressed as

$$g = \frac{V - \chi_{Pt} - (\phi_b - \phi_s) - d\chi - \phi_1}{e}$$

where g is the Galvani potential

6.4.7.3. To obtain some idea of the relation between the potentials measured and the potential across the water dipole, we must make some estimate of the other terms in the equation. In fact χ_{Pt} , $(\phi_b - \phi_s)$ and ϕ_1 will all be small. Bardeen and Brattain⁽¹²⁾ have shown that $(\phi_b - \phi_s)$ under the experimental conditions we have been using, amounts to only about 0.02v. We can also conclude that as the oxide layer was no thicker than about 10^{-5} cm., and so could not support much of the space-charge region, the voltage drop in the oxide ϕ_1 is very small. Under open-circuit conditions, the voltage across the system is then almost entirely due to the water dipole term $d\chi$. When the system is brought to equilibrium, the Volta potential will approximate to $\frac{1}{e}(E_{Pt} - E_{Ge}) + d\chi$

The exact value of the Galvani potential is not known but the term $\frac{1}{e}(E_{Pt} - E_{Ge})$ may amount to 1 or 2 volts, so that the total potential across the gap may be 1.5 to 2.5 volts.

6.4.7.4. It is generally agreed that water is adsorbed on a germanium surface only to the extent of one or two monolayers. We have assumed a monolayer for our calculation of the number of water molecules adsorbed on the surface. It should be noted that the system described here does not agree well with the picture given by other workers of adsorbed water on n-type germanium, Refs. (76)(79). It is common to describe a system of positively charged states, created by the water adsorption, with the energy bands in the semiconductor bending downwards, to give a negative space-charge region. The picture we have described appears to be a better approximation to the truth.

6.4.8. Discussion of experimental results

6.4.8.1. The form of the results shown in Figure 20 shows little dependence on the type of germanium used or on the thickness of the oxide layer. This suggests that the observed voltages arise mainly from the interaction of the moist ambient with the outer oxide surface. For the elementary case of a single layer of orientated water dipoles adsorbed on the surface the voltage developed is given by Gauss's theory as:

$$V = 4\pi Nq.d.$$

where V = voltage

N = number of adsorbed water molecules/cm².

q = electronic charge.

d = charge displacement (= about 10^{-8} cm. for singly ionized oxygen).

Thus, if V is taken to be about 500 mV,

$$N = 2.8 \times 10^{13}.$$

and for 700 mV, $N = 3.9 \times 10^{13}$.

6.4.8.2. The agreement between this figure and the values quoted (75)(76) for the density of slow surface states is quite good. Thus, it may be passable to explain the observed voltages by a mechanism involving the adsorption of orientated water dipoles by slow surface states. To do this, it is necessary to postulate feasible energy level diagrams to correspond with the experimentally observed behaviour formally given in Figure 20. Unfortunately little quantitative data is available pertaining to the band structure of oxide covered semiconductors, so any argument has to be mainly qualitative in nature.

6.4.8.3. Commencing with the assumption, that the initial source of the observed voltage is the adsorption of orientated water dipoles by slow surface states, the main observations requiring explanation are; the slow decay curves, the rapid rise curves following a short-circuit and the effects of an applied field. It is relevant, at this point, to describe the deviations, mentioned earlier, in the normal cycle. Referring to Figure 20, it was found that a momentary short circuit at point a on the decay curve resulted in a rapid recovery whilst a similar procedure at point b was followed by a slow recovery. The general behaviour is shown in Figure 24. The point of interest is, that, despite the considerable disturbance at point b, the voltage finally returns to the normal decay curve. These observations are considered to indicate that the source of observed voltage during decay is an electronic charge, and not adsorbed water. After the initial adsorption of water it is assumed that the dipole is completely ionised and the slow acceptor surface state becomes negatively charged. Since the hydrogen atom is essentially located at the electrostatically zero reference point it must be considered

to remain neutral. At point b it is assumed that all this water has been adsorbed from the surface thus leaving it negatively charged.

6.4.8.4. In considering the rate of decay it is necessary to look at the main regions across which charge may migrate. These are; (i) the space charge in the germanium, (ii) the surface states at the Ge/Ge₂O₃ oxide interface, (iii) the oxide itself, (iv) the oxide/ambient interface and (v) the gap between this last and the platinum reference electrode. The time constant of the observed decay curve is in the order of several minutes which is unlikely to arise from processes occurring in regions (i) and (ii). Also, region (v) can be discounted since, at the measured impedance of ca. 10^{10} ohms, this has a time constant in the order of milliseconds. This leaves regions (iii) and (iv) as possible sources of the slow decay process. Now, that the bulk oxide itself is a good electronic conductor is amply demonstrated by the fact that copious electrolytic reduction can be performed at a Ge/Ge oxide electrode in solution. Thus, charge transfer across the oxide will be a fast process and cannot be the cause of the observed decay. This reasoning is strongly supported by the fact that the observed decay is apparently independent of the thickness of the oxide film. It must be tentatively concluded, therefore, that the oxide surface with its negatively charged slow surface states is the region of interest. It seems possible that the observed decay is, in fact, a direct measure of the rate of relaxation of the slow states. The main features of the experimental results are illustrated in Figures 21-23. In these diagrams the full width of the chart corresponds to 1.0 volt whilst the spacings marked by the hour, in fact, correspond to 80 seconds. In Figure 21, at point A, the ambient was changed from moist to dry oxygen. At point B a momentary application of about 700 mV external field gave rise to a second decay curve. In figure 22 moist ambient was introduced at point A and the resultant potential growth is shown. At point B the system was momentarily shorted after which the rapid, oscillatory recovery is clearly seen. Point C shows the affect of a 900 mV external field whilst at point D the decay curve commences as a result of changing to a dry ambient. Figure 23 shows the behaviour of the n-type specimen after it had been boiled in sodium hypochlorite solution for a few minutes. At points A, B and C the system was short circuited and the rapid, but non-oscillatory, nature of the recovery is shown. At point D the ambient was changed to dry oxygen after which a markedly step-wise decay curve resulted.

6.4.8.5. When the system is brought into equilibrium by an external short-circuit, we can calculate the charge on each electrode on either side of the gap. In our experiments, the gap is virtually the dipole layer of water molecules itself, as the glass fibre probe extends to the germanium surface. The charge on each electrode is given by

$$Q = v/4\pi d.$$

where v is the Volta potential

If we take v as the difference of the work functions it will be approximately 6.5-4.8, or 1.7 volts. The distance d would be approximately 10^{-8} cm. for completely ionized oxygen. Calculation gives a value for $Q = 9 \times 10^{13}$ electronic charges per cm^2 .

Thus the original negative charge in the surface states, of 3 or 4×10^{13} per cm^2 , is completely neutralized and converted to a large positive charge. This positive charge would have two effects, firstly to attract a higher concentration of water molecules, which are predisposed to yield up electrons, and secondly to develop a negative space-charge, or accumulation region, in the semiconductor. The situation is illustrated in Fig. 19B. On removing the short-circuit, an excess of water molecules are associating with the charged surface, but this excess positive charge is rapidly removed by conduction through the oxide layer and germanium.

The oxide surface is temporarily provided with a much higher concentration of water molecules, and it is also possible that the positive charge may have temporarily created a higher concentration of surface states. The water dipole system then builds up very rapidly and overshoots its normal level, because of the higher concentration of adsorbed water. The situation is rapidly restored by a loss of water, within a few hundred milliseconds, and the potential falls rapidly. In many instances there is again another overshoot in the downward direction, the reason for which is less clear. The second overshoot may be associated with an adjustment of the space-charge region, which for a brief period has developed a high non-equilibrium concentration of holes, due to the migration of the positive charge; the response of the second overshoot would depend to some extent on the diffusion rate of holes through the oxide layer. The absence of overshoot in some samples may indicate a low hole mobility in the oxide layer of those samples.

6.4.8.6. The application of an excess positive potential to the platinum in the presence of water, increases the field across the dipole layer, which is rapidly discharged on removal of the potential. In some experiments it was observed that the potential returned rapidly to a slightly higher level than before, suggesting that the increased field had created more surface states at the oxide surface, or filled some higher energy levels.

6.4.8.7. The application of a positive potential to the platinum electrode in the absence of water vapour creates a similar condition at the germanium surface to the effect of water molecules, by inducing a negative charge in the slow surface states. On removing the potential, we observe a slow decay, due to the relaxation time of these states. Section 6.4.6.8. shows that the applied potential will appear entirely across the gap.

6.4.8.8. The origin of possible potentials in the 10 volt region still remains unsolved, but it is interesting to note that if the charge density we have observed in the water dipole layer existed across an oxide layer of only 10^{-6} cm. thick, a value of 10 volts would be obtainable.

6.4.8.9. The decay curves obtained on removing the water vapour from the oxygen flow indicate that the slow states normally present on the oxide surface have relaxation times of the order of 300 to 500 secs. A stepped structure is found in the decay curves for many samples, but the definition of these steps varies considerably and their interpretation would have to await further investigation: it is possible that such discontinuities might represent the relaxation of states at different energy levels.

6.4.8.10. Potential growth rate when moisture was admitted to the oxygen flow was fairly rapid (taking about 80 secs.) but there was usually a much smaller slope towards the end of the growth curve, sometimes containing steps, suggesting a slow final orientation of the water layer. The growth and decay times are more rapid than those observed by Bardeen and Brattain ⁽¹²⁾ probably because of the longer response time of their apparatus.

6.4.8.11. A few comparative experiments were made on 200 ohm-cm. p-type silicon, platinum, brass and stainless steel. The silicon showed some similarities to germanium in that it was possible to charge the surface states by applying an external field, and obtain a decay curve. The potential attained in wet

oxygen was much lower, suggesting a small adsorption of water, but this may have been the result of incorrect surface preparation. Further work would be required before any meaningful comparisons could be made. Platinum, as expected, showed no potential under dry or wet ambients. Both brass and stainless steel gave indications of growth and decay curves: this is very interesting and points the way to the possibility of studying oxide films on metals by this technique.

6.4.8.12. Etching procedures had some influence on the potentials obtained, higher values generally being produced by sodium hypochlorite treatment, which gave a visible oxide film. The curves obtained with surfaces prepared by chemical etching contained more small irregularities than those obtained with surfaces prepared by anodizing. The difference suggests that chemically etched surfaces give patchy oxide films, while anodized films have a more ordered and uniform structure: this conclusion is also supported by the appearance of the films.

6.4.8.13. Harman et al.⁽¹⁷⁾ have recently carried out an interesting measurement of water-induced surface states on silicon, using porous graphite electrodes and a pulse technique. They arrive at a figure of $5 \times 10^{12}/\text{cm}^2$. Our preliminary tests indicated that the density on silicon was less than on germanium and it would be useful to carry out comparative experiments by our method.

7.0 CONCLUSIONS

7.1 The final products of the photooxidation of benzaldehyde at a germanium surface are benzoic acid and dibenzoyl peroxide. No indications of other possible products, such as benzil or benzoin have been found.

7.2 Repeat experiments of surface potentials on germanium have not in general confirmed the high potentials previously recorded, except in a few isolated experiments. An analysis of the operation of the backing-off circuits, used for the indirect measurement of potentials, has shown that misleading results can be obtained. The maximum voltages previously obtained are estimated to be of the order of 10 volts.

7.3 The use of a glass fibre probe in conjunction with a direct-reading electrometer, with an input impedance of 10^{15} to 10^{16} ohms has enabled accurate and reproducible measurements of surface potential to be made. The voltage obtained in wet oxygen is normally in the range 500 to 700 mV, depending to some extent on the oxide film on the germanium,

7.4 The time-voltage curves obtained for the experiments under various conditions have provided useful information on the properties of the slow states at the germanium oxide-gas interface. The maximum potential obtained, shown to be due to an ionized layer of water molecules, corresponds to a slow state density of 3 to 4×10^{15} per cm^2 . The rate of decay of the charge remaining in the slow states after the removal of water molecules indicates relaxation times of 300 to 500 seconds in most of the samples tested.

7.5 Some unusual features observed on the curves include a step-like structure in some of the decay curves, and an oscillatory behaviour after a momentary short-circuit (to bring the system to thermodynamic equilibrium). The step structure might be associated with different energy levels in the spectrum of states, while the oscillatory behaviour is produced by an adjustment of the non-equilibrium concentration of water molecules at the surface and changes in the space-charge region.

7.6 No great differences have been observed between n-type, p-type and intrinsic germanium, which indicates that the surface potential behaviour is almost entirely a function of the oxide layer. It is possible from the variations in the time-voltage curves between different samples to make qualitative deductions about the structure and carrier mobility in the oxide film.

7.7 Surface recombination measurements on germanium samples treated with irradiated benzaldehyde show a small but definite decrease in surface recombination after treatment. Together with indications of increased surface barrier height, given by the rectification experiments, the decrease in surface recombination velocity shows that the benzaldehyde treatment may be a good finishing process for the surface of semiconductor devices.

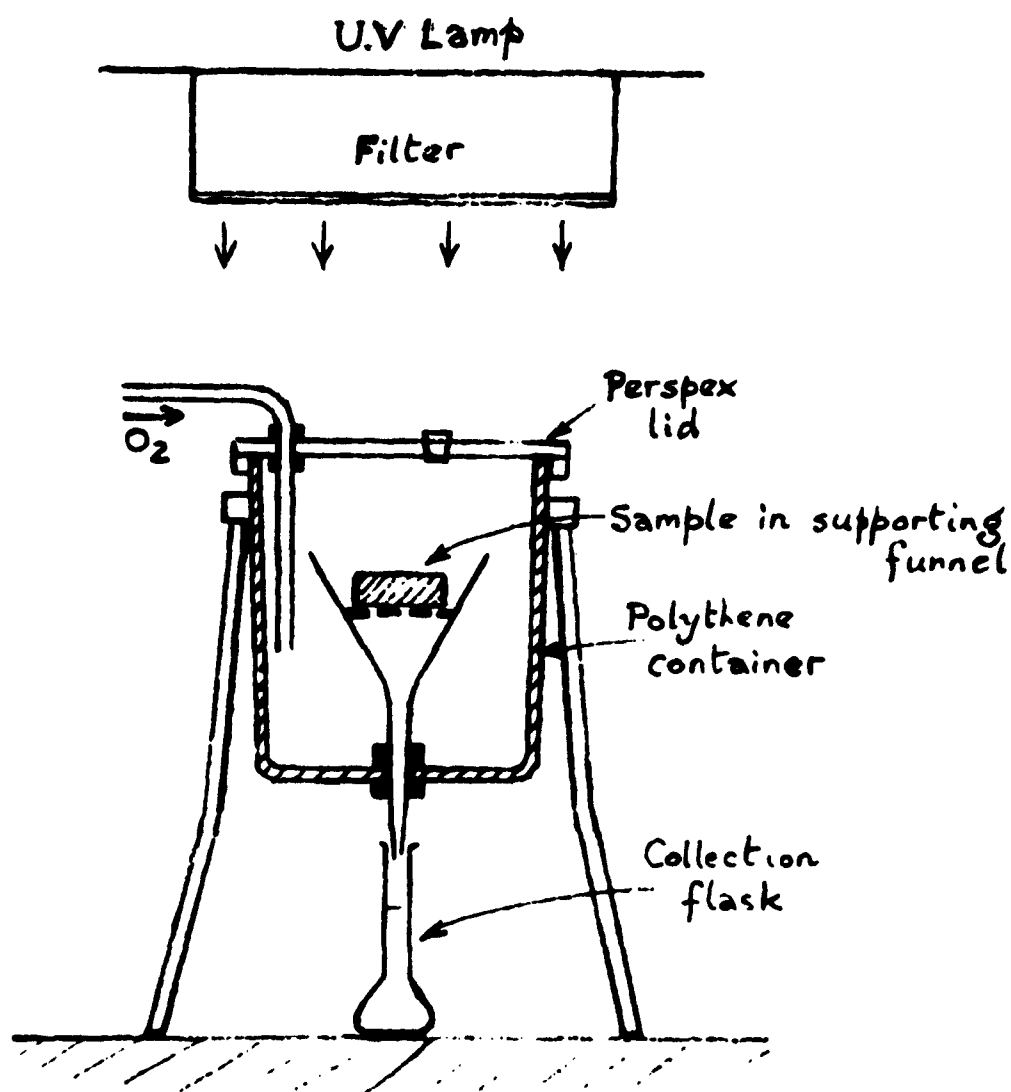
7.8 Increases in the photocurrent from a surface barrier diode have been obtained by the application of a film of benzaldehyde. The increase in efficiency has been correlated with the quantum efficiency of the photochemical reaction, by the principles of charge-transfer catalysis.

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Irradiation Apparatus.

FIG. 1

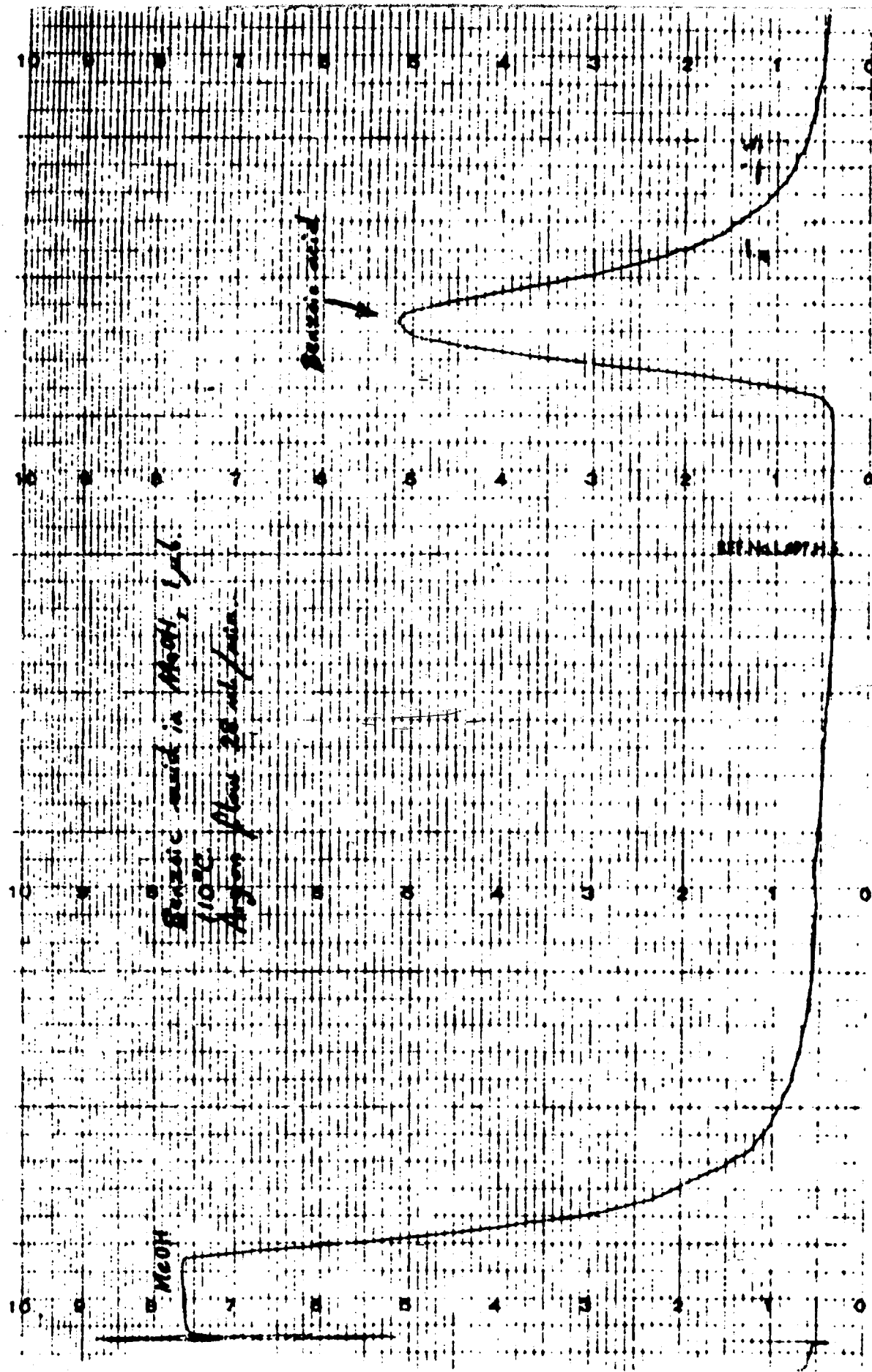


FIG. 3.

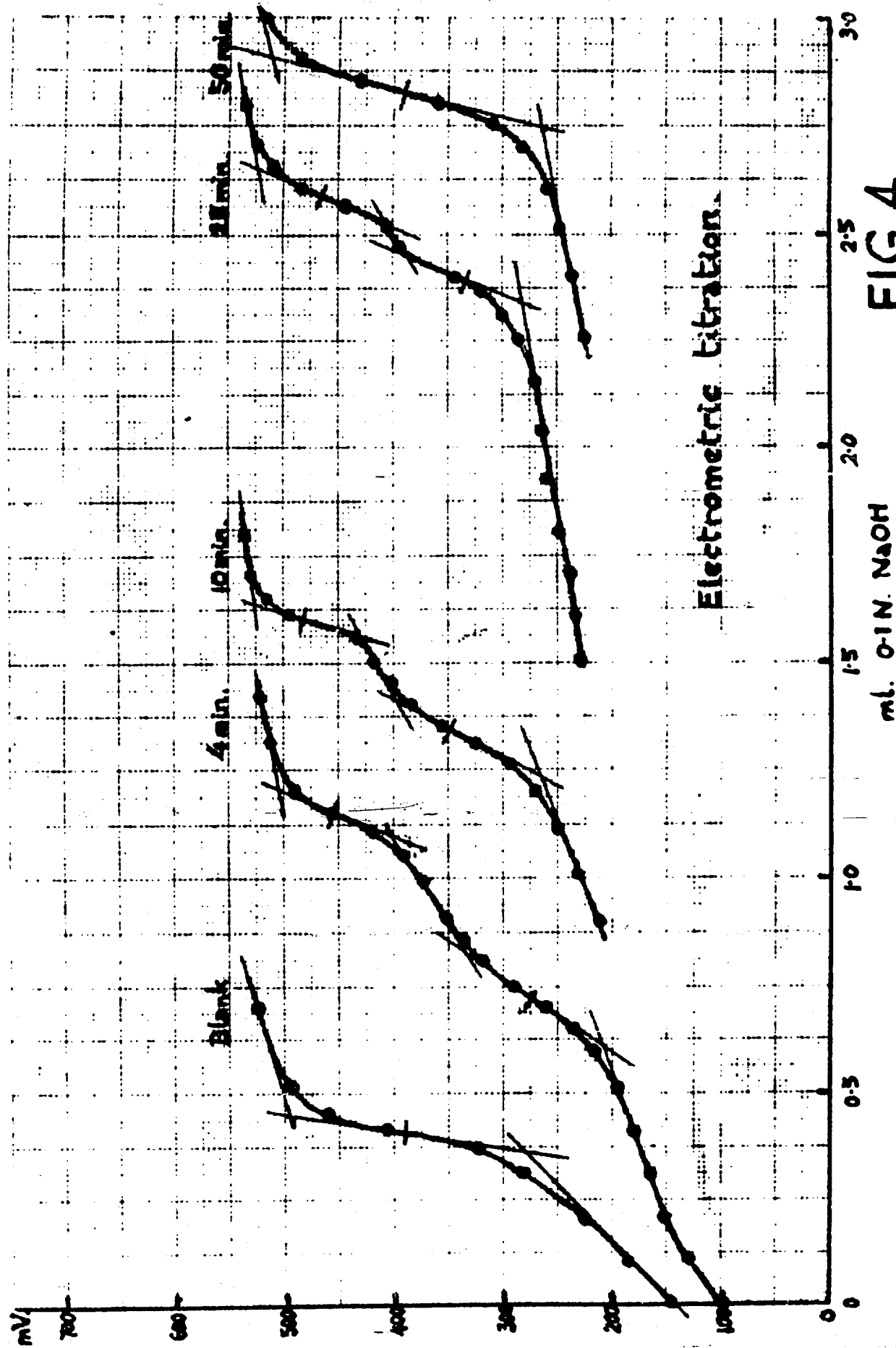


FIG.4.

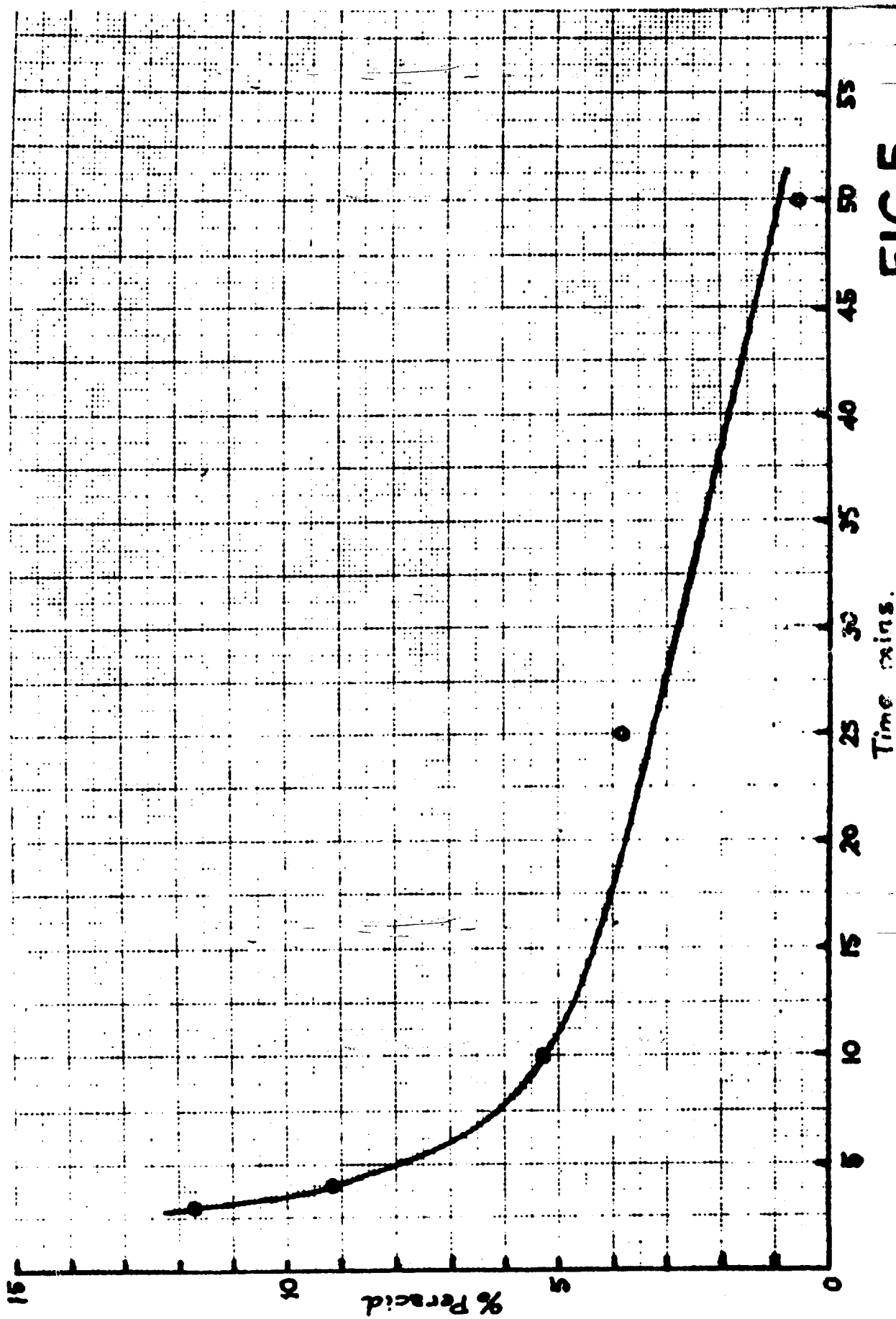
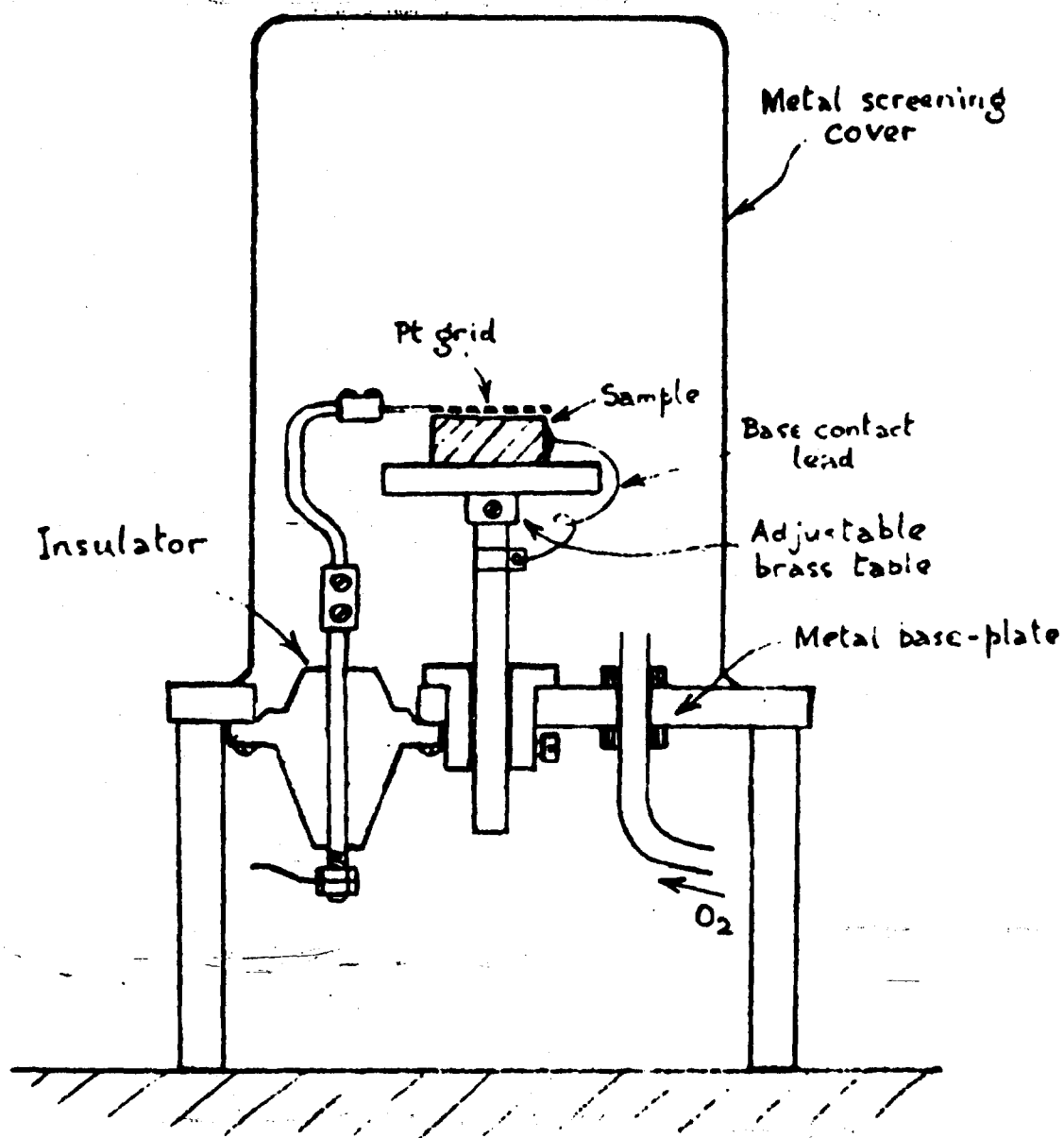
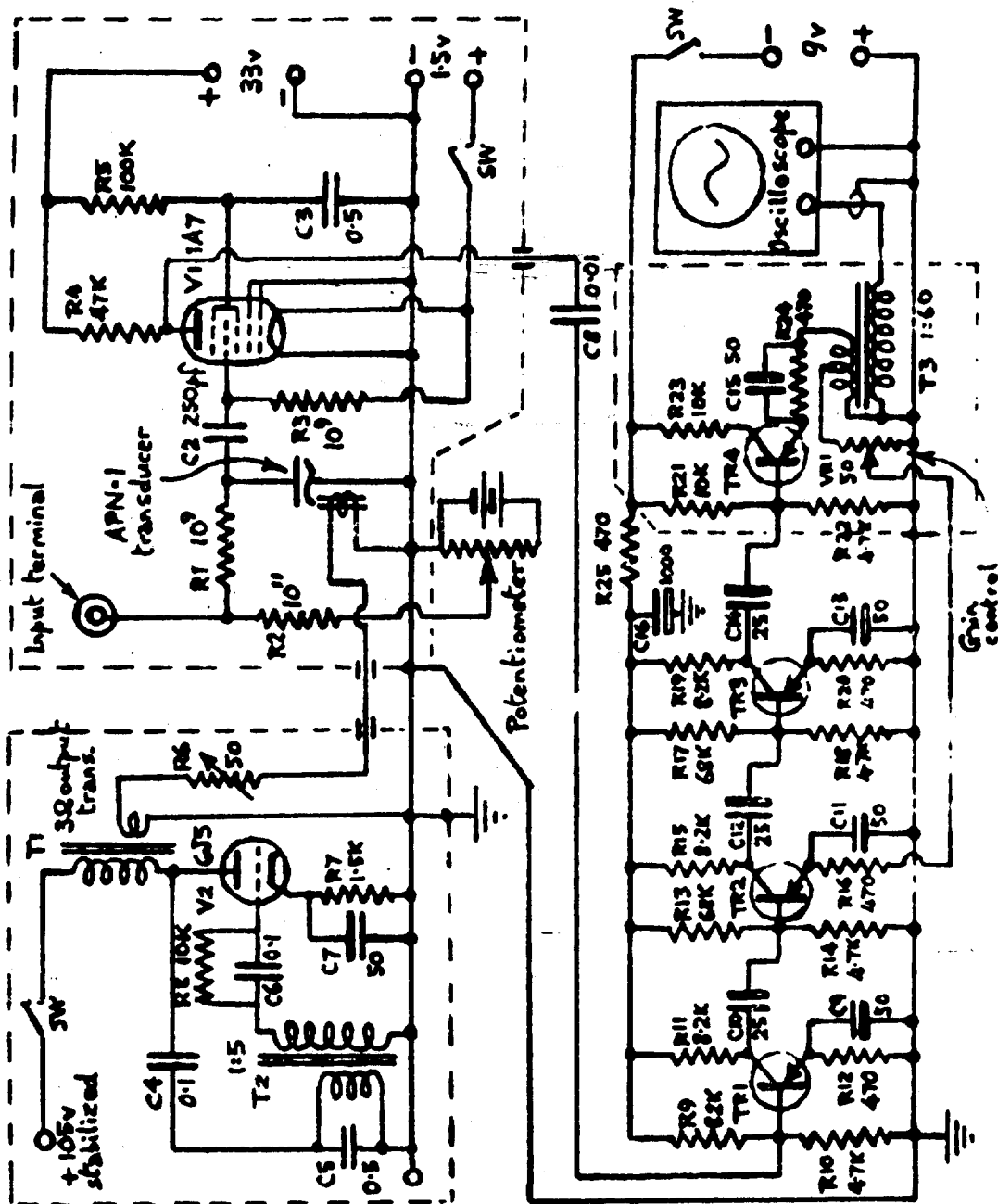


FIG.5.



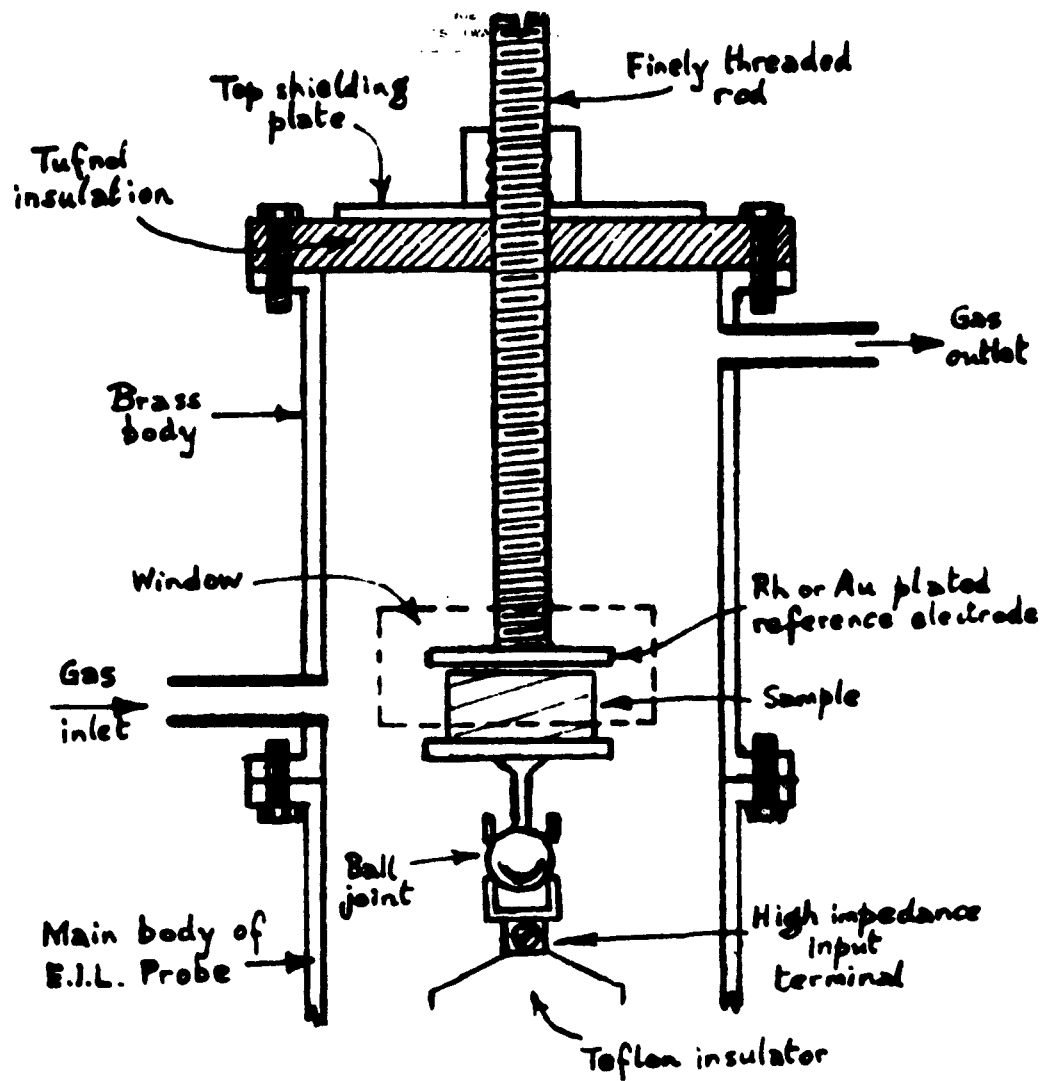
Contact Potential Apparatus.

FIG. 6.



All fixed resistors are 1/4 watt.
 TR1, 2, 3, 4 transistors are Edison XBN13
 TR1 preferably a low noise unit.

FIG. 7.
 Contact Potential Amplifier.



Electrode Assembly for E.I.L. Electrometer.

FIG.8.

Biassing Circuits.

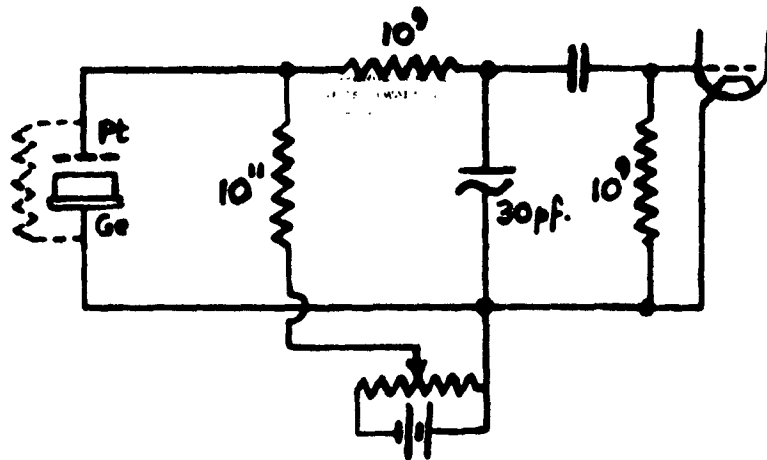


FIG. 9.

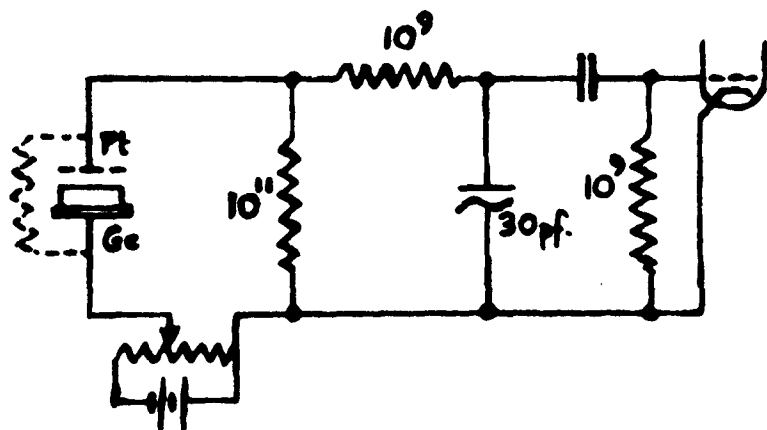


FIG. 10A

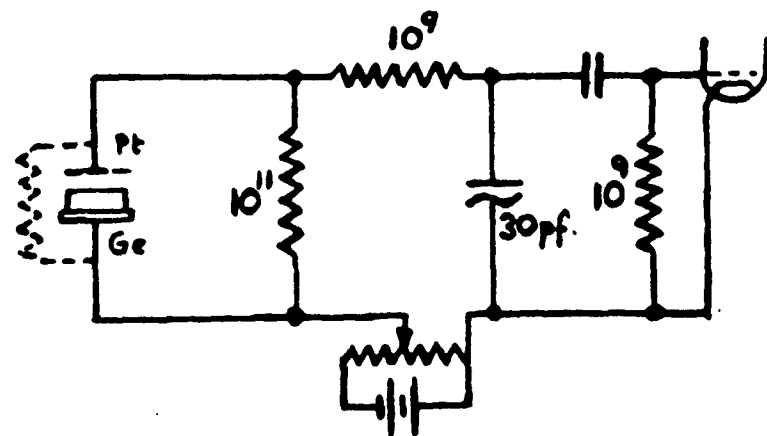


FIG. 10B

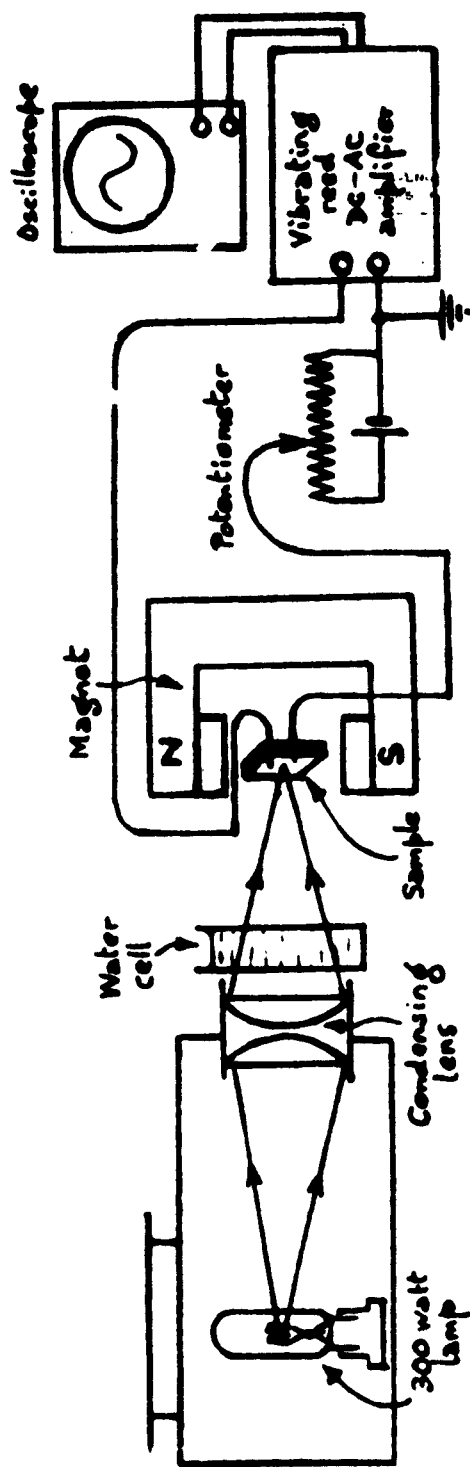


FIG.11. Photodetromagnetic Effect Apparatus.

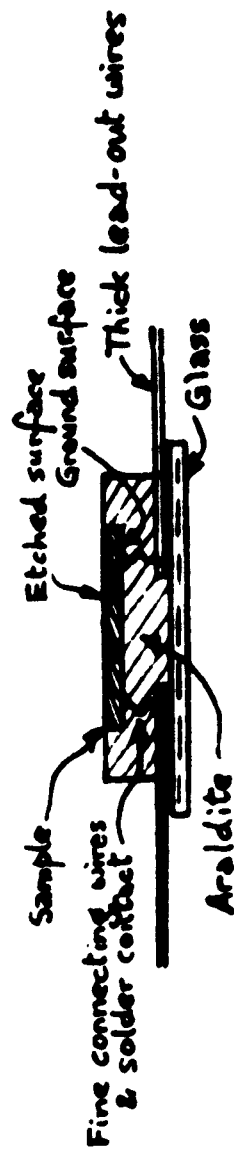


FIG.12. P.E.M. Sample Section.

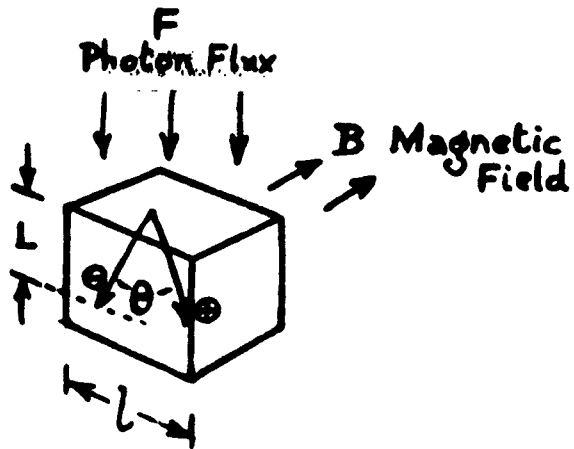


FIG.13. Schematic P.E.M. Effect.

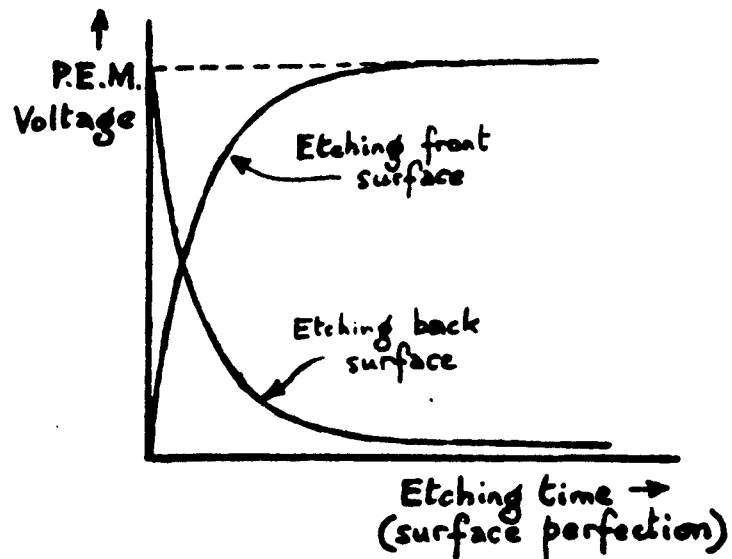


FIG.14. P.E.M. Voltage & Etch Time

Illuminated Photocell.

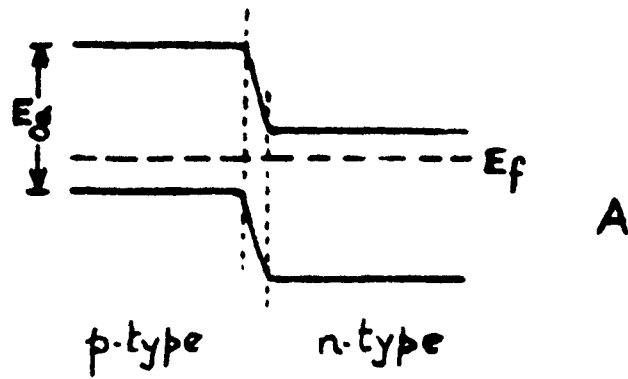


FIG.15.

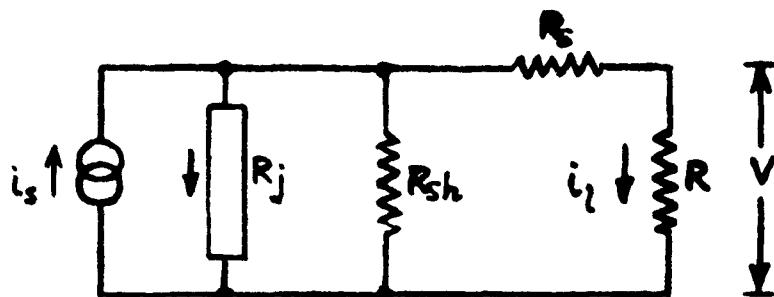
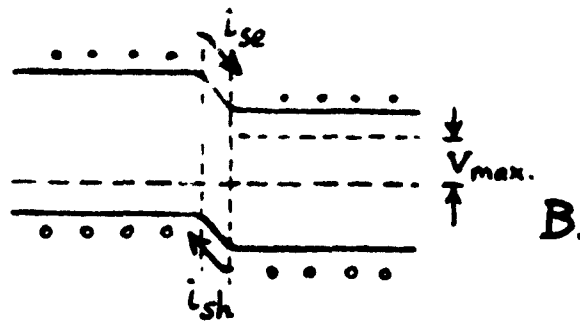


FIG.16.

Equivalent Circuit of Illuminated Photocell

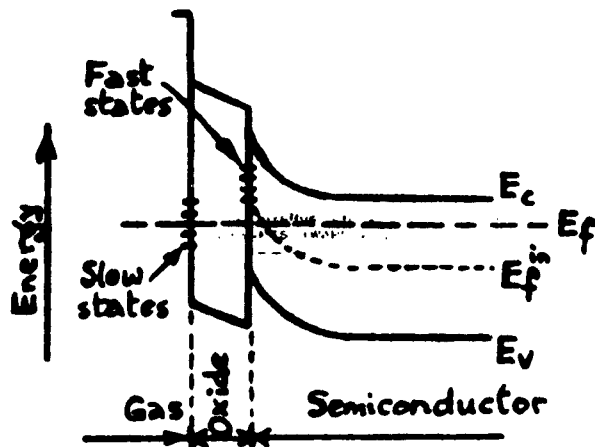


FIG.17.

n-type Semiconductor with Surface States.

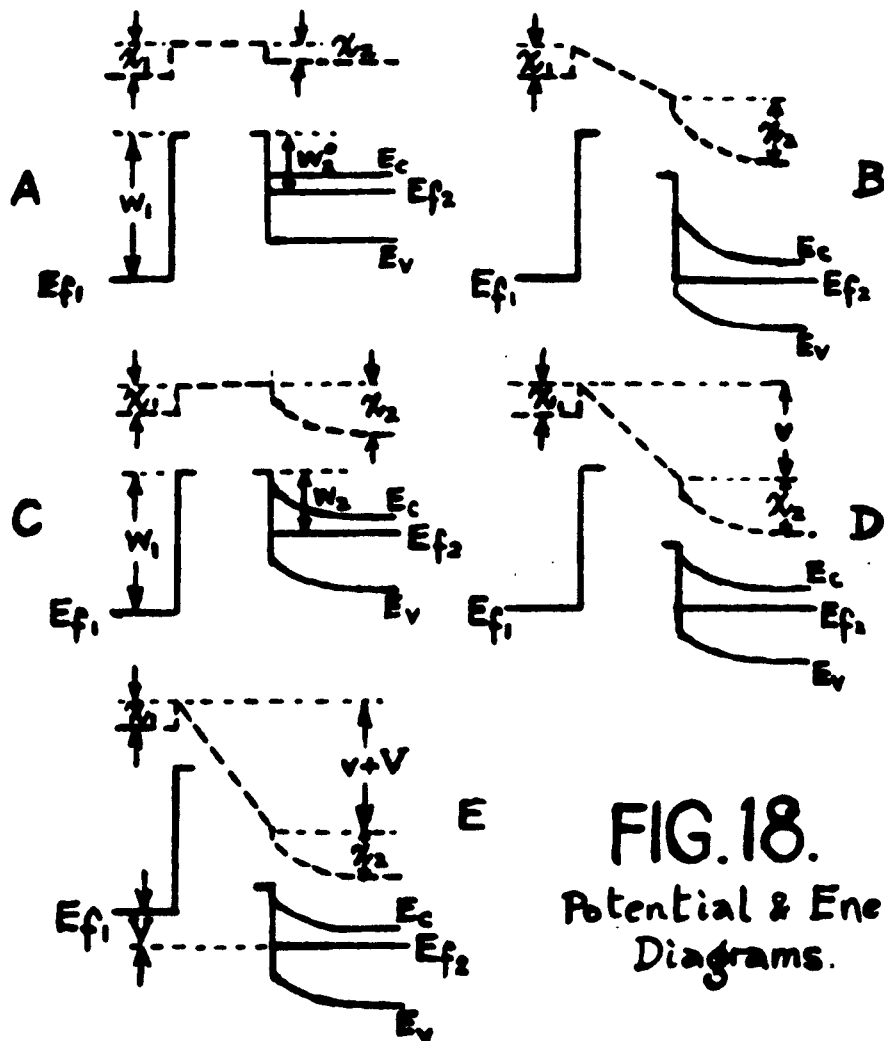


FIG.18.
Potential & Energy
Diagrams.

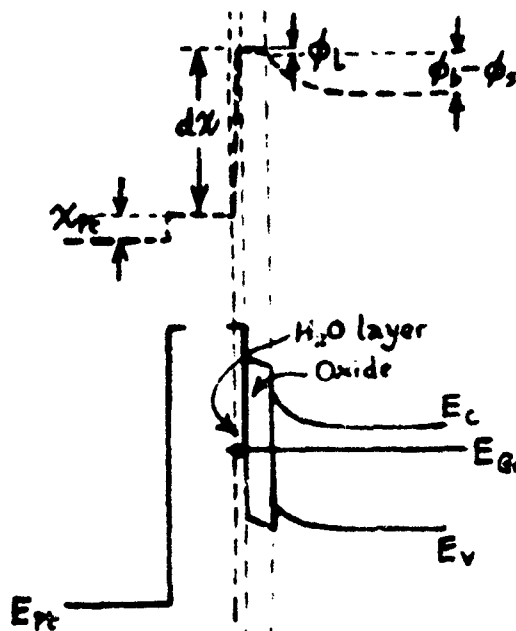


FIG. 19A
Before
equilibrium

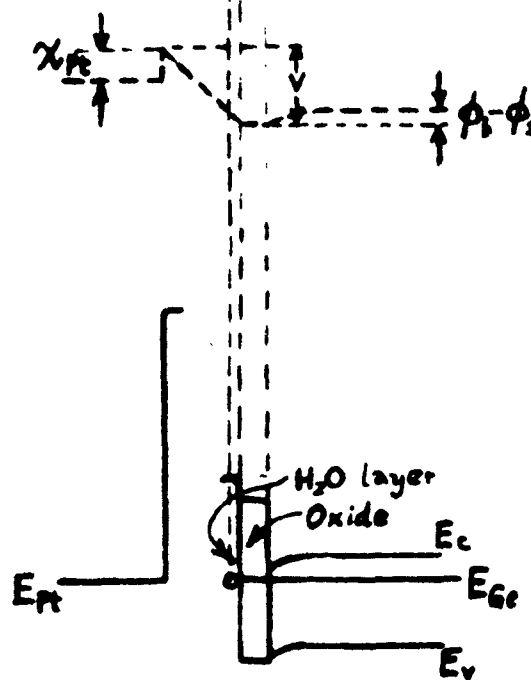


FIG. 19B
After
equilibrium

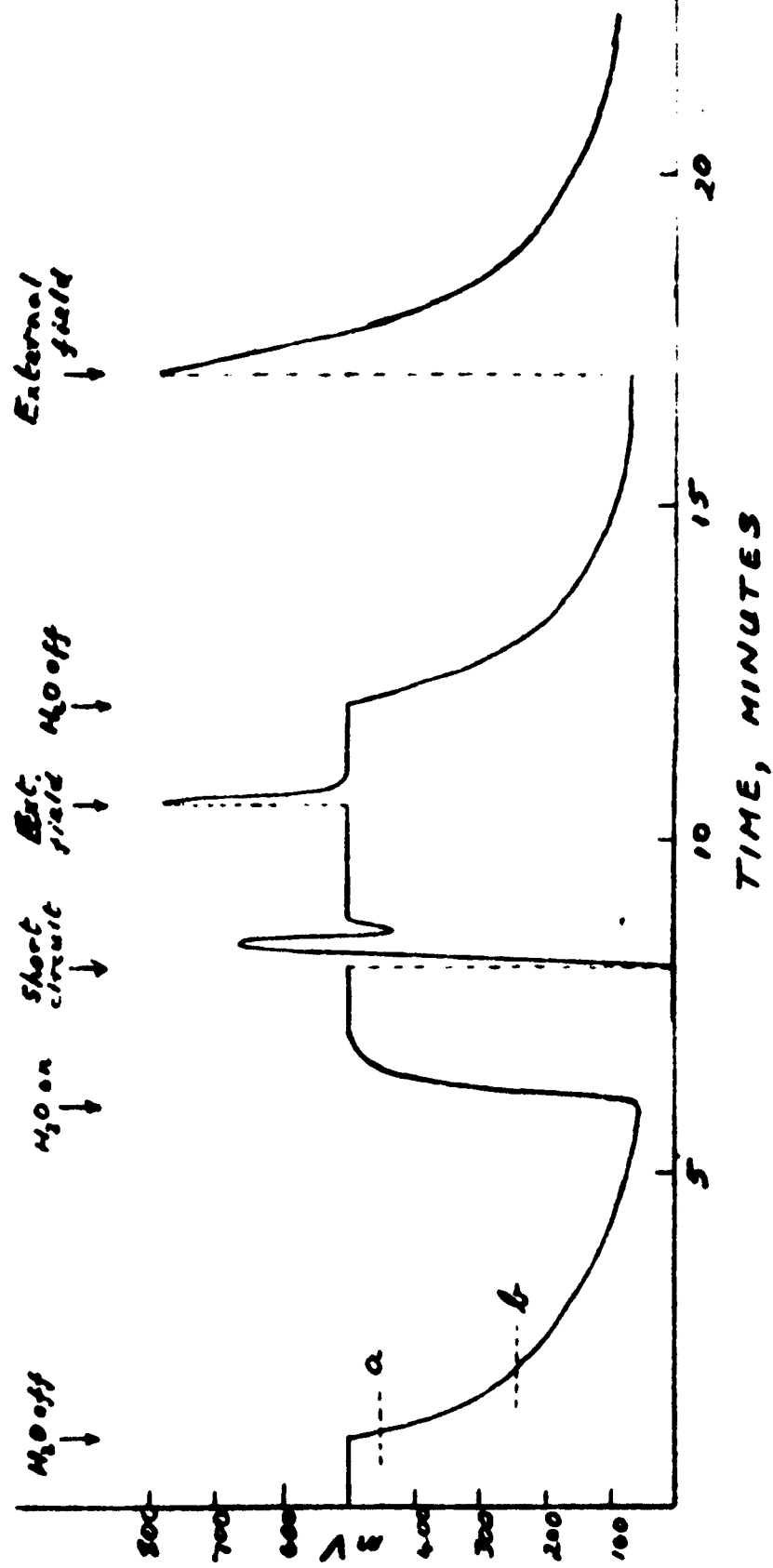


FIG. 20

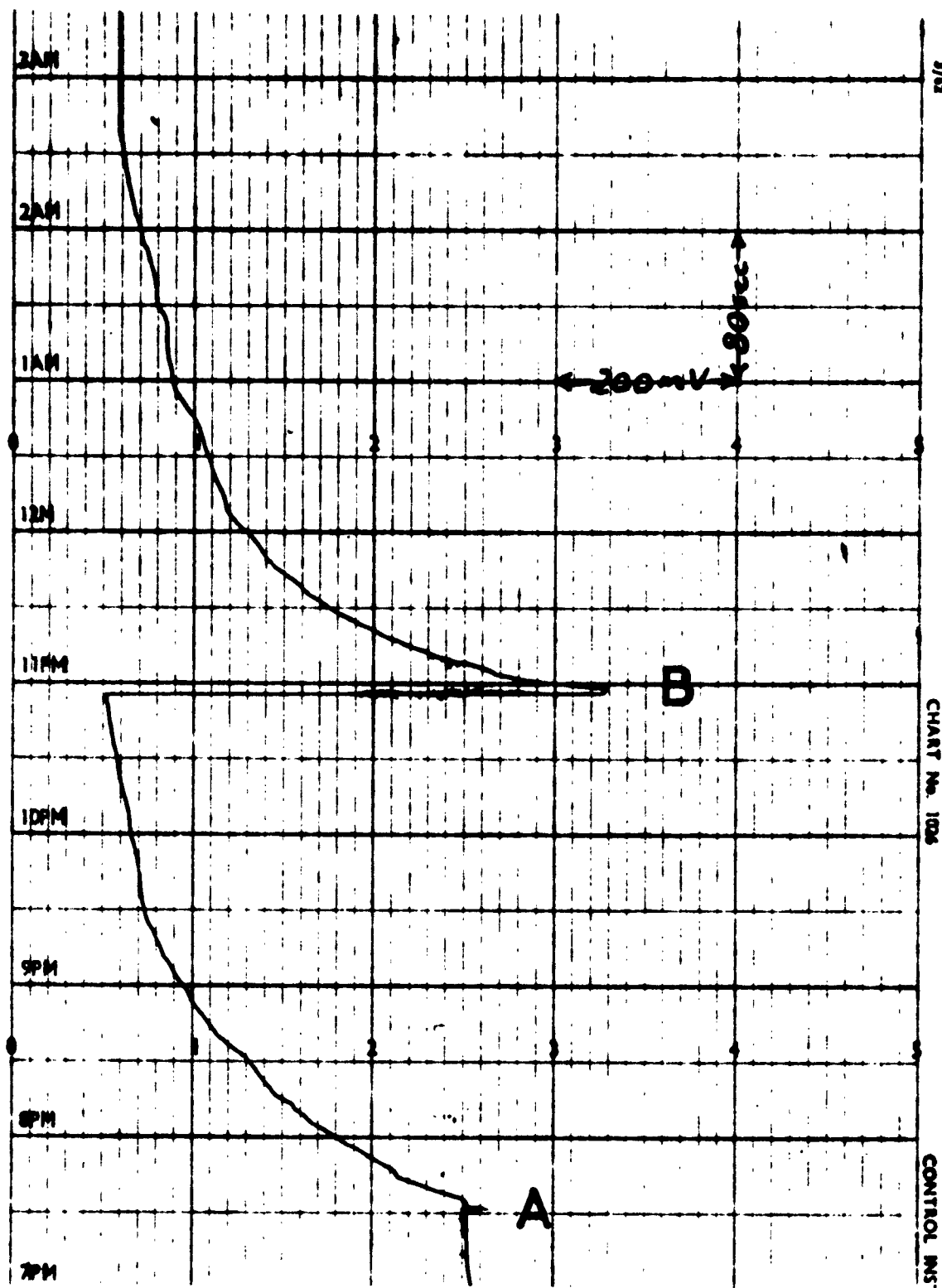


FIG. 21 n-Type Ge. Anodised

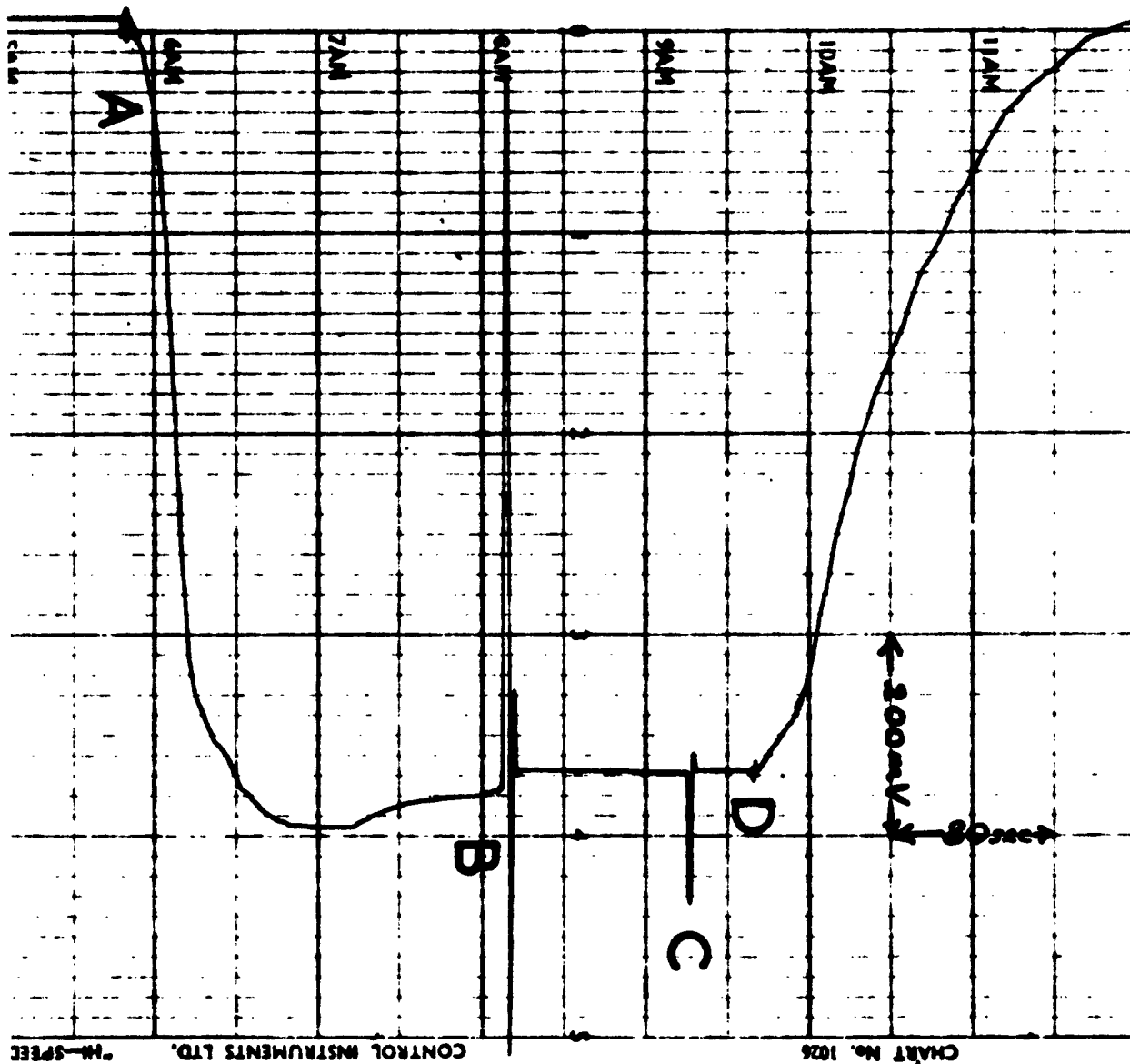


FIG. 22 p-Type Ge. Anodised

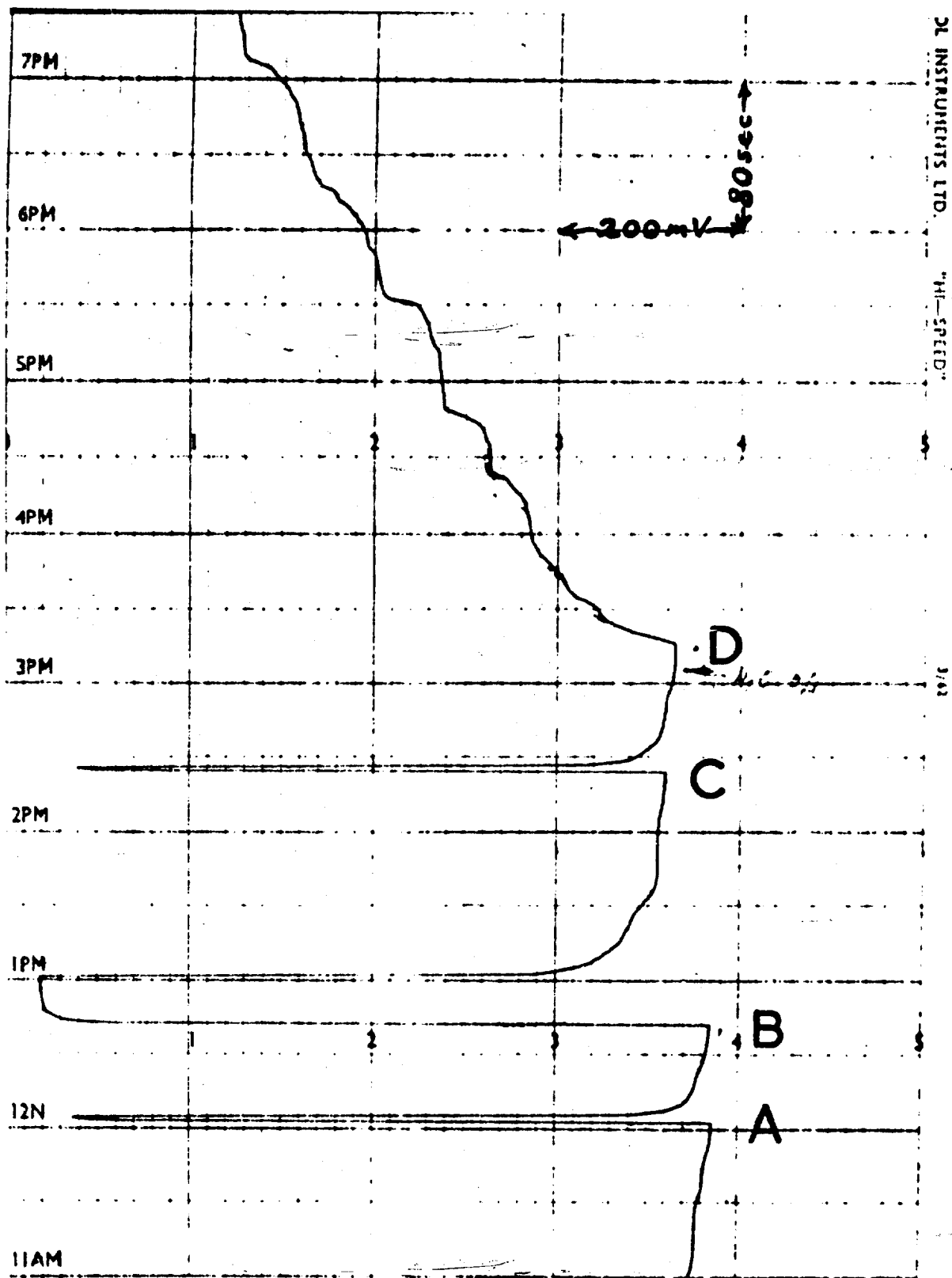


FIG. 23 n-Type Ge. NaOCl

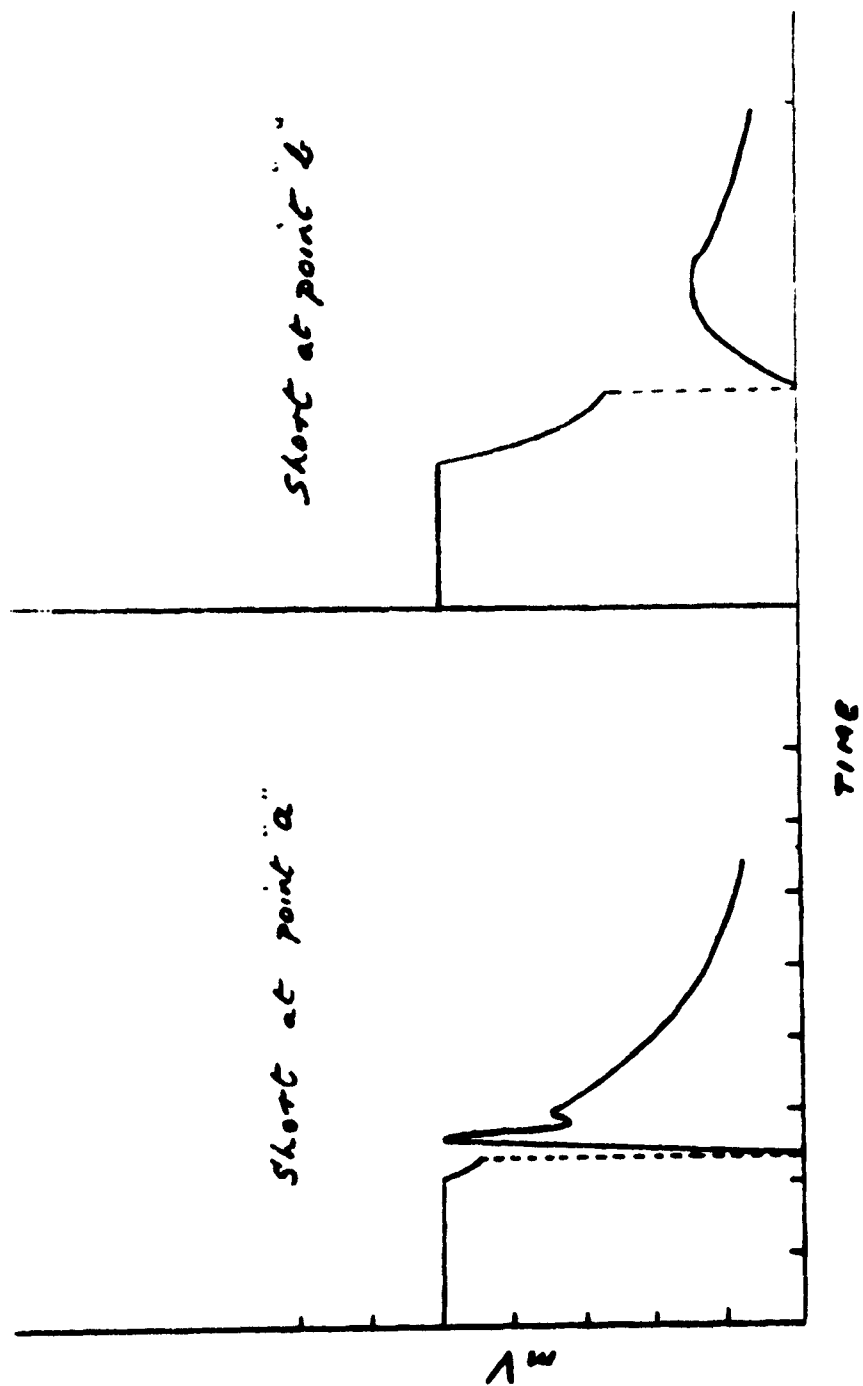


FIG. 24

Summary of personnel utilized during the reporting period

Principal Investigator, J.A. Radley, M.Sc., F.R.I.C., F.S.D.C.	300 hours
Assistant Principal Investigator, G. Elliott, B.Sc., F.R.I.C.	1250 hours
Research Assistant, J.G. Gibson, B.Sc.	1000 hours
Research Assistant (Graduate standard)	850 hours

<u>Expense for materials expended:</u>	£560
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<u>Property acquired during contract period at direct contract expense:</u>	Nil
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signed:

J.A. Radley.....